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Development of Innovative Remedial Methods for PBT-Contaminated Sediments in the Great Lakes Drainage Basin

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Need to be anchored

abrasion - thick enough

Sand on gravel

Spikes!

Development of Innovative Remedial Methods for PBT-Contaminated

Sediments in the Great Lakes Drainage Basin

Executive Summary

Persistent, Bioaccumulative Toxin (PBT)-contaminated **sediments** pose health risks due to contaminant movement up the food chain to fish and humans. PBTs include lead, mercury, **PCBs**, PAHs and certain other organic contaminants. Our goal was to test a new method to cut off contaminated **sediments** from the food chain.

Our method is to cover "hot spots" in the stream or lake bed with an anchored geotextile layer to stop biointrusion and erosion. The permeable geotextile fabric is covered with sand, gravel and/or cobbles to cut off benthic organisms from feeding in the contaminated **sediments**, and prevent erosion of these **sediments** while allowing groundwater inflow. This method can be **combined** with biochemical methods to hasten contaminant degradation beneath the geotextile.

Two geotextiles used as biointrusion barriers were evaluated in laboratory permeameters containing **sediments**; one of the geotextiles was also evaluated in Gull Creek, Michigan. The field trial included four 3 x 3 meter patches in the creek bed. Two of the patches were covered with a geotextile topped with 1-3 cm of anchoring sand and pea gravel; the other two patches were controls. Six months later one of the controls was sampled, and a geotextile patch was sacrificed to permit sampling underneath.

Results of lab and field trials to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in **sediments**. Only 4.26 ± 2.47% of the organisms present moved through the geotextiles ($t_g = 3.25$, $P < 0.05$) in lab Trials 2-4. In Gull Creek, benthic invertebrate density was reduced by 93.5% under the geotextile-covered patch relative to the control after six months of coverage.

Ozone and CHEMOX® were both successful in greatly speeding up the breakdown of **PCBs** and other persistent contaminants like PAHs in laboratory tests. **Treatment** with **ozone** and CHEMOX® resulted in greater than 90% removal in one month of both **PCBs** tested. The amounts of oxidants required and the time needed for detoxification both increased as the fraction of natural organic matter in the contaminated **sediments** increased. The method also requires spreading the oxidants thoroughly through the contaminated **sediments**. Application of these oxidants will be most successful in **sediments** contaminated with organic chemicals with low proportions of organic matter and into which the oxidants can be disseminated well.

These preliminary tests of this new method for reducing health risks from contaminated **sediments** suggest that the geotextile biointrusion barrier has great promise and should be further evaluated in full-scale field trials. The **chemical** oxidants (especially CHEMOX®) may be **combined** with the geotextile barrier in future field trials, and should be used in separate trials focusing upon detoxification of dredge spoils prior to disposal.

Development of Innovative Remedial Methods for PBT-Contaminated Sediments in the Great Lakes Drainage Basin

Introduction

Current remedial methods for PCB-contaminated **sediments** in river and lake bottoms and harbors and shores are woefully inadequate. The most frequently chosen remedial method is dredging. Dredging is sometimes effective, particularly in the case of grossly contaminated **sediments**, but has four serious drawbacks. (1) Where and how can we dispose of the dredge spoils? Typical answers are incineration (which creates dioxins) and/or dumping in somebody's

back yard (often in a poor and/or minority community). (2) Additional spreading of contamination and resulting risk to human health and the environment is often induced by disturbing and resuspending the **sediments** during dredging. (3) Dredging never removes all contaminated **sediments** (90% removal would be an optimistic goal in most cases). Thus dredging leaves a source (about 10% of contaminant mass) in place and more exposed due to removal of the overlying **sediments**. (4) Dredging completely disrupts habitat and ecological values of streams and lakes. A relatively new alternative to dredging is subaqueous capping in place, or armored stream or lake bottoms. This "management in place" results in an underwater landfill, a toxic waste site gift-wrapped for future generations to inherit. It is hard to believe that these are the best methods we have developed to deal with contaminated **sediments**.

To develop a better remedial method for contaminated **sediments**, it is first helpful to recognize four basic principles. 1. Streams and lakes are hydrologically active water bodies that connect with and exchange water with groundwater aquifers. Many surface water bodies would dry up without groundwater inflow. Blocking water flow through lake and river **sediments**, such as would occur in subaqueous capping, is not acceptable. 2. **PCBs** and many other persistent contaminants found in **sediments** tend to adsorb strongly to those (primarily fine-grained) **sediments**. To control the contaminants, we must control the **sediments**. Yet the usual fate of sedimentary deposits is further erosion and transport and redeposition. 3. These persistent chemicals degrade slowly if at all. Yet biodegradation in place, if it could be accelerated, would likely be the most feasible solution to this problem of broadly disseminated pollution. 4. These chemicals adsorb not only to fine-grained **sediments**, but often to the fatty tissue of biota. Many organisms contact and adsorb these contaminants as they burrow through or stir up **sediments** looking for food. At higher levels of the food chain, the contaminants they adsorb may be biomagnified and represent a threat to human health as well as the environment.

We propose a new method for managing in place **sediments** contaminated with PBTs, including **PCBs**, PAHs, lead and mercury. This method could be called anchored permeable geotextile biointrusion barriers. Briefly, the concept is that the contaminated **sediments** should be managed in place using a permeable geotextile layer to prevent biointrusion by benthic organisms or sediment-mining fish. This biointrusion barrier is held in place, or "anchored", against erosion by water currents using sand, gravel and/or cobbles as required by the currents. There are many different geotextiles, some of which have been developed to stabilize stream banks against erosion, others for draining leachate from underneath landfills. The specific geotextile fabric chosen, and the thickness and grain size of the anchoring layers would be determined on a site-specific basis, taking into account the size of the predominant benthic organisms to exclude from beneath the geotextile barrier and the water currents to be overcome.

The anchored permeable geotextile biointrusion barrier would be an improvement over the subaqueous capping in place method because it allows water to continue to feed the surface water body. It would also allow biodegradation of organic contaminants such as **PCBs** and PAHs to slowly continue, in contrast to a subaqueous cap which would cut off **sediments** from the surroundings and also likely terminate biodegradation. Nevertheless, an approach relying upon natural biodegradation of **PCBs** would not remove the contaminant mass at an adequate rate to satisfy most host communities.

An important addition to the anchored permeable geotextile biointrusion barrier would be a method to accelerate the rate of PCB biomineralization. If such a method could be deployed along with the biointrusion barrier, then the investment of our society's resources in emplacing the biointrusion barrier could be justified because it would eventually result in contaminant removal from the biosphere. This would be a method of remediating contaminated **sediments** worthy of research and development.

We propose that the rate of PCB biomineralization may be enhanced by the addition of **ozone** or by a proprietary oxidant, CHEMOX®. **Ozone** can work at neutral pH to chemically dechlorinate many chlorinated organics. The breakdown products of PCB congener dechlorination may be more biodegradable. Hence, we proposed first conducting a laboratory study to test the merits of this idea. If the lab tests are promising, we wish to study this idea in concert with our biointrusion barrier to see if, together, they could provide a reasonable solution for remediating some PCB-contaminated **sediments** in lakes and rivers.

Of course, no remedial method will solve all problems. Usually several remedial methods are used in concert to deal with real-world problems. It is likely that this proposed method would be most applicable to exposed and/or shallow

sediments near shore that are vulnerable to erosion. It would probably be applied particularly to PCB hot-spots rather than to entire river or lake bottoms. If the PCB and/or other contaminant concentrations were so high as to result in oily fluids oozing from the **sediments**, dredging would be a more appropriate remedy. The geotextile biointrusion barrier could also be used without oxidants underneath as a temporary or even semi-permanent stabilizing measure to contain **sediments** contaminated with lead, methylmercury, radionucleides and/or **PCBs** until a permanent remedy becomes possible.

This study was conducted in two separate parts. One research effort focused on the feasibility of geotextiles as biointrusion barriers. The other effort examined the efficacy of **chemical** oxidants for accelerating PCB degradation in contaminated **sediments**. These two efforts are reported separately below, each with its own abstract.

I. Using Geotextile Biointrusion Barriers to Remediate Contaminated Sediments

A. ABSTRACT

Contaminated river, lake and harbor **sediments** are one of the more challenging remedial legacies we must face in order to reduce risk to human health and the environment. In most locations, these risks are entirely due to contaminant movement from these **sediments** up the food chain to fish and their predators, including humans. Common contaminants include mercury, lead, **PCBs** and other organic chemicals that adsorb to fine **sediments** and the organic materials they contain. The goal of this study was to devise and test an in-situ method to stabilize the contaminated **sediments** and cut them off from the food chain.

The method we propose is to place an anchored geotextile layer over hot spots in the stream or lake bed to serve as a barrier to biointrusion and erosion. A geotextile is a permeable fabric used on or within soils that is made of plastic fibers selected for durability, strength and other design objectives. The geotextile fabric is covered with enough sand, gravel and/or cobbles to hold it in place on top of contaminated **sediments**. The geotextile plus anchoring granular layer prevents erosion and remobilization of the contaminated **sediments**, cuts off benthic organisms and demersal fish from living and feeding in the contaminated **sediments**, and holds the **sediments** in place while allowing groundwater to continue feeding the stream or lake. The biointrusion barrier is an alternative to dredging and landfilling the contaminated **sediments**, the most common remedial alternative, and to covering them with an impermeable HDPE liner, another alternative that creates an underwater landfill and cuts off groundwater base flow. It can be **combined** with biochemical methods to hasten contaminant degradation beneath the geotextile, and/or with chemicals that enhance contaminant sorption to the geotextile.

The effectiveness of two geotextiles as a biointrusion barrier was evaluated in laboratory permeameters containing **sediments** from Gull Creek, Michigan; one of the geotextiles was also evaluated in Gull Creek. The lab experiment followed a completely crossed factorial design involving two types of nonwoven geotextile patches, two types of stream **sediments** (sandy vs more organic, finer stream bed **sediments**), and live organisms vs killed controls. Combinations of treatments were randomly assigned to trials and permeameters. The field trial included four 3 x 3 meter patches in the bed of Gull Creek. **Sediments** from each of the patches were sampled to determine density of benthic organisms. Then two of the patches were covered with a geotextile layer topped with 1-3 cm of anchoring sand and pea gravel; the other two patches served as controls. Six months later one of the controls was sampled, and a geotextile patch was sacrificed to permit sampling underneath. The other geotextile patch will be sacrificed in 10/02 and all four patches will be sampled again.

Results of trials conducted to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in Gull Creek **sediments**. After some slight methodological flaws were discovered in Trial 1, only 4.26 ± 2.47% of the individuals present moved through the geotextile ($t_g = 3.25$, $P < 0.05$) in Trials 2-4. All of the animals that moved through the geotextiles in Trials 2-4 were roundworms or oligochaete annelid worms which, in general, have very small cross-sectional areas. The geotextiles were quite effective barriers against the

movement of the remaining infaunal taxa present in the permeameters, including copepods, ostracods, gammarid amphipods, and chironomid larvae. Surprisingly, the thinner geotextile was a better barrier to benthic invertebrates than the heavier, thicker geotextile used in the field test. The field test results to date largely support the laboratory test results. The four patches were initially (10/01) dominated by copepods, amphipods, oligochaetes, and roundworms. After a winter (4/02), the control patch sampled had a lower density consisting primarily of roundworms (31.1%), copepods (28.8%), and oligochaete worms (15.8%). The sediments under the geotextile patch contained only roundworms (65.2%) and ostracods (34.8%). Benthic invertebrate density was reduced by 93.5% in the geotextile-covered patch relative to the control after six months of coverage.

These preliminary tests of this new method for reducing health risks from contaminated sediments suggest that the geotextile biointrusion barrier has great promise and should be further evaluated in full-scale field trials.

b. compariSON OF different geotextiles for suitablility

Geotextiles are permeable fabrics of plastic fibers used within soil masses to accomplish certain functions: separation, reinforcement, filtration, drainage, and/or containment. Plastic fibers are used because of long life, excellent durability and strength. Particular polymers can be chosen as a fiber source to produce a geotextile ideally suited for a given application. There are currently at least 100 specific application areas for geotextiles. Our research is proposing a new application for geotextiles: to be used on top of contaminated stream sediments as a biointrusion barrier, a stream sediment filter and erosion barrier.

There are two main types of geotextiles: woven and non-woven. Non-woven geotextiles are almost always chosen over woven geotextiles for applications involving filtration because they have smaller and more uniform openings. However, a few people feel that woven geotextiles can perform better in creating graded filters in the long run because they are less prone to clog.

There are hundreds of different geotextiles available from several domestic and foreign manufacturers. To help choose which ones to test, we attended two international meetings in spring 2001. We visited with manufacturers and with many of their customers. These geotextile experts gave us many different recommendations as to which geotextiles to use. However, they did agree that there were a few experts in the use of geotextiles whom we should contact. Tops on everyone's list was John Price of Price & Company in Wyoming, Michigan. John is the elected president of the International Erosion Control Association, one of the two meetings we attended. John provided us with test samples of several of the Amoco geotextiles he supplies to users, primarily non-wovens. We also obtained test samples from several other manufacturers. John told us (as did several other experts) that he had seen geotextiles used to cover contaminated sediments in streams and ponds, but neither he nor anyone else we met had ever heard of the idea of using geotextiles to prevent biointrusion into contaminated sediments. He suggested several non-wovens that were strong enough and had been successful for him in the past. Therefore, we decided to test those first.

C. MATERIALS AND METHODS

We conducted laboratory tests of various geotextiles. We set up six permeameters containing sediment samples from Gull Creek. These 5-cm thick sediment samples were covered with one of two geotextiles, followed by 2.5-3.0 cm of clean fine white sand. The permeameters were connected with a constant-head water source flowing into the bottom and upward through the sediments, the geotextile and overlying anchoring sand layer. The permeameters were placed inside a refrigerator to replicate Michigan field conditions prevalent at the time of sediment sampling. Our goals in these experiments were to determine which geotextiles: 1) prevent organisms from moving up through the geotextile into the overlying sand, 2) clog or remain permeable to water, and 3) allow sediments to move into the sand. Each trial using 6 permeameters ran for one week. The experiment followed a completely crossed factorial design involving two types of stream sediments (sandy vs more organic, finer stream bed materials), two types of geotextile patches, and live organisms vs killed controls. Combinations of t Treatments reatments were randomly assigned to trials and permeameters.

We wanted to test two non-woven geotextiles (Amoco #4512 and Amoco #4553) as sediment filters and biointrusion barriers in a controlled laboratory setting, which would simulate water flow in a gaining stream system. Therefore, the permeameters were designed so water would move upward through sediment, then through a geotextile into the overlying water column.

In the area where the test patches were placed there are two main types of sediment, a fairly firm, sandy type near the center of the channel and a very soft, organic rich type near the banks of the channel. We wanted to repeat the combinations of the two sediment types, two geotextile types and two geotextile function types (sediment filtration and biointrusion barrier) three times. A random number table was developed to randomize the sampling. Four trials were conducted, with six permeameters used in each trial.

Acrylic permeameters were used which were in five segments with the bottom segment alone and the middle two and the top two segments permanently connected. An influent hole was made in the bottom segment and an effluent hole was made in the top segment of each permeameter. The influent hole had a ⅛ inch Tygon tube leading into it from a holding tank with a constant water level elevation (or head) fed by tap water. The tank had six tubes attached to the bottom of the tank; each went to a permeameter. Air was bubbled through the water in the tank to remove chlorine. Chlorinated tap water would have adverse effects on organisms, such as death. The residence time of water in the holding tank varied for each set of trials due to the different permeabilities of the sediment combinations in each trial. However, the average residence time was found to be approximately 9.5 minutes. Since organisms were found to move through geotextile in three of the four trials, the bubbling of air through the water removed enough chlorine to sustain life. The effluent hole in each permeameter had a ⅛ inch Tygon tube leading to a filter, which collected the sediment that passed through a geotextile.

Sediment cores were collected directly into the lower pair of segments used in the permeameters. The segments were sealed with stoppers and promptly returned to the laboratory. Cores that were to be used for a permeameter testing a geotextile's efficacy as a biointrusion barrier went directly into a refrigerator, which had a thermostat control placed at 40° F. The experiment was conducted from March through early May of 2002 when the stream and sediment temperatures were very close to this constant temperature. This prevented shock and death of organisms contained within the sediment samples due to rapid increase in temperature. Cores that were to be used for a permeameter testing a geotextile's efficacy as a sediment filter were boiled for 15 minutes to kill any organism in the core to prevent them from getting through the geotextiles and collecting on the filter that was weighed for sediment.

Prior to collecting the cores, filters were weighed on an analytical scale, which has an accuracy of 0.0001 grams. In addition, the specific geotextile that is to be used is placed in the permeameter. On the bottom of the top two sections of the permeameters, a metal disk containing a screen US sieve size 6 is placed in the opening. A geotextile is then placed on the sieve in the opening and sealed around the edge with silicone caulk to prevent anything circumventing the geotextile. The sieve acts as a brace to the geotextile to prevent bowing.

To assemble the permeameters, a metal disk containing a screen US sieve size 270 was placed in the bottom opening of the segments containing the core to support the core and prevent it from falling into the bottom segment. A bead of waterproof adhesive was placed on the top of the bottom segment. The bottom and middle segments were then joined. Similarly, the middle and top segments were attached. In the case of the biointrusion barrier permeameters, 2.5-3.0 centimeters of fine-grained sand was placed in the top segments after the permeameter was fully assembled. This was done to provide a habitat that would sustain organisms that got through the geotextiles. Caps were placed on the permeameters, which were then placed in vice-like vertical frames located in a refrigerator.

Once the permeameters were in place, the influent water tubes and the effluent water tubes were attached using waterproof adhesive. Geotec 0.45 micron glass fiber filters and Whatman GFC 1.0 micron glass fiber filters were positioned at the end of the effluent tubes from permeameters to collect sediment. During the first two trials the Geotec filters were used. It was found that these filters did not maintain their integrity during and after the drying process. Therefore, during trials three and four the Whatman filters were utilized. Once everything was ready, the laboratory-grade demineralized water was turned on and continued to run for seven days

When each week-long trial was over, the water of each permeameter was allowed to collect in separate containers for ½

hour. The water was measured in a graduated cylinder, and flow rates for each permeameter were determined. The permeameters were then taken apart. The segments of the biointrusion barrier permeameters were carefully separated, with the fine white sand above the geotextile placed into one container and the sediment core placed into another container. The **sediments** were preserved so organisms did not degrade and could be enumerated. The filters, which had been collecting sediment from the effluent tubes, were placed in a drying oven at 105 °C for 24 hours. The filters were weighed following drying to determine the mass of sediment collected on them.

In October, 2001, we installed two test patches in an uncontaminated stream. This was part of a test of the geotextile's ability to prevent biointrusion. We sampled four, 3 by 3 meter square patches of stream **sediments** in Gull Creek near Kalamazoo, Michigan, for benthic density. Five core samples (area = 5.07 cm^2 per core) were taken in each patch and preserved with 10% formalin with rose Bengal stain added to facilitate separating invertebrates from the sediment. Two of those areas were subsequently covered with non-woven geotextile patches. The other two areas were experimental controls. The patches were held in place against the current by a 1—2 cm anchoring layer of sand and pea gravel. We have since gone back to inspect the patches and measure the stream velocity. In late April 2002 we sacrificed one randomly selected patch to sample underneath for benthic density. We also measured the benthic density in one randlomly selected control area. Five core samples were taken from each area. In Oct. 2002 we will sample underneath the other geotextile patch as well as in the other three areas to determine the benthic population density.

D. RESULTS AND DISCUSSION

Results of permeameter trials conducted to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in Gull Creek **sediments** (Table 1). Over all trials, the percent of individuals that moved across the geotextile barrier was significantly greater than 0 (mean ± SE: 6.0 ± 1.9; $t_{14} = 5.0$ on arcsine square root transformed proportions, $P < 0.001$). However, in the first trial, we suspected that many of the individuals moved around the geotextile rather than through it, and we modified the permeameters accordingly. Performance of the geotextiles was markedly improved in the remaining trials; only 4.26 ± 2.47% of the individuals present moved through the geotextile ($t_8 = 3.25$, $P < 0.05$). All of the animals that moved through the geotextiles in Trials 2-4 were roundworms or oligochaete annelid worms which, in general, have very small cross-sectional areas. The geotextiles were quite effective barriers against the movement of the remaining infaunal taxa present in the permeamteres, including copepods, ostracods, gammarid amphipods, and chironomid larvae.

Table 1. Percent of animals crossing the geotextile barrier in four laboratory permeameter trials.

Trial	**Permeameter**	Number Below Geotextile	Percent Crossing Geotextile
0	1	32	8.5
	2	25	3.8

	3	15	6.2
	4	29	0
	5	13	18.7
	6	12	14.2
2	2	22	0
	3	16	0
	4	23	8
	6	61	8.9
3	1	11	21.4
	3	17	0
	5	17	0
4	1	18	0
	2	7	0

Field tests of the geotextiles largely support the results of laboratory permeameter experiments. Control and geotextile-covered patches contained a diverse infaunal assemblage in October 2001, immediately before geotextile patches were installed. In all patches, the infaunal community was dominated by copepods, amphipods, oligochaetes, and roundworms (Table 2). Total invertebrate density ranged from 71,441 to 234,057 individuals/m^2. In April 2002, total invertebrate density in the control patch sampled was 69,862 individuals/m^2, with copepods, roundworms, and oligochaete worms accounting for 28.8, 31.1, and 15.8%, respectively, of all individuals. By contrast, the geotextile-covered patch contained only 4359 individuals/m^2 and 2 taxa (roundworms: 65.2%; ostracods: 34.8%) (Table 2). Thus, benthic invertebrate density was reduced by 93.5% in the geotextile-covered patch relative to the control. These results suggest the geotextile provides a highly effective biointrusion barrier. In addition, there was close agreement between the laboratory and field studies in that roundworms, which were more likely to move through the geotextile than other taxa, were best able to maintain populations below the field geotextile barrier. Nonetheless, roundworm density in the geotextile-covered patch was 86% less than that observed in the control patch, indicating that even these animals were strongly affected by the geotextile barrier.

Table 2. Mean invertebrate density (number/m^2) in field patches						
	Oct-01	Oct-01	Oct-01	Oct-01	Apr-02	Apr-02
	Control	Control	Geotextile	geotextile	Control	Geotextile
Taxon	Patch 1 (upstream)	Patch 2 (downstream)	Patch 1 (upstream)	Patch 2 (downstream)	Patch 1 (upstream)	Patch 2 (downstream)
Crustacea						
Copepod (& harpacticoid)	20524.4	80518.8	22103.2	21708.5	20129.7	0
Nauplii	1184.1	19735	0	0	0	0
Cladocera	0	10656.9	0	0	3947	0
Ostracod	3947	3947	1578.8	789.4	6709.9	1578.8
Isopod	6315.2	9867.5	1578.8	4341.7	789.4	0
Amphipod	12630.4	20129.7	33944.2	23287.3	1973.5	0
Insecta						
Chironimidae	11446.3	31181.3	15393.3	5920.5	2368.2	0
Ephemeroptera	1184.1	1973.5	394.7	789.4	0	0
Leptoceridae	0	0	0	394.7	0	0
Zygoptera	0	789.4	0	0	0	0
Elmidae	0	394.7	0	0	0	0
Diptera (misc)	394.7	0	0	0	394.7	0
Other						
Oligochete	13419.8	20129.7	7894	5131.1	11051.6	0
Clam	3157.6	0	394.7	0	789.4	0
Roundworm	26050.2	34733.6	44995.8	9078.1	21708.5	2960.25
Water bear	1184.1	0	0	0	0	0
Collembola	394.7	0	0	0	0	0
TOTAL	101832.6	234057.1	128277.5	71440.7	69861.9	4539.05

D1. target species affected by geotextile barrier

We have applied geotextile barriers to soft **sediments** (sands and finer) because such **sediments** are expected to be the most contaminated. Organisms that live on or in such **sediments** in streams, rivers, and lakes fall into two general

categories: the meiofauna (operationally defined as those animals retained on a 40-μm sieve but pass through a 500-μm sieve) and macrofauna (retained on a 500-μm sieve). Because the maximum pore size in all of the geotextile fabrics that we are testing is < 250 μm, we are most concerned with the ability of the fabrics to constrain movement of the meiofauna. Stream and river meiofauna communities are usually dominated by rotifers (Rotifera), harpacticoid and cyclopoid copepods (Crustacea: Copepoda), small (young) chironomid larvae (Diptera: Chironomidae), naidid and enchytraeid oligochaetes (Annelida: Oligochaetae), and nematodes (Nematoda). All of these groups are well represented in soft **sediments** in Gull Creek (Table 2) and the Kalamazoo River. In addition, ostracods (Crustacea: Ostracoda) are common in many locations. Gammarid amphipods (Crustacea: Amphipoda) often dominate the soft sediment macrofauna in the Kalamazoo River basin, but even juvenile gammarids are too large to pass through geotextile pores, so we do not anticipate the need to be concerned about their movements (although they will be included in both the field and laboratory tests). Because they prey upon microbial communities in the **sediments** and are themselves preyed upon by stream macrobenthos and fish, the meiofauna are important in energy flow in aquatic systems and in linking microbes to large invertebrate predators and fish. Thus, breaking this link should markedly affect rates of PCB bioaccumulation in higher trophic levels.

We predicted that meiofaunal densities below geotextile test patches in Gull Creek would decline rapidly with time since installation and stabilize at very low levels, relative to controls. This prediction has been strongly supported by work conducted thus far (Table 2). Therefore, it appears that the geotextiles should break the microbes – meiofauna – large invertebrates and fish linkage, effectively isolating contaminated **sediments** from the food chain.

E. SUMMARY

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Results of lab and field trials to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in **sediments**. Only 4.26 ± 2.47% of the organisms present moved through the geotextiles ($t_g = 3.25$, $P < 0.05$) in lab Trials 2-4. In Gull Creek, benthic invertebrate density was reduced by 93.5% under the geotextile-covered patch relative to the control after six months of coverage.

These preliminary tests of this new method for reducing health risks from contaminated **sediments** suggest that the geotextile biointrusion barrier has great promise and should be further evaluated in full-scale field trials.

No remedial method, including this one, will solve all problems. Usually several remedial methods are used in concert to deal with real-world problems. It is likely that this proposed method would be most applicable to exposed and/or shallow **sediments** near shore that are vulnerable to erosion. It would probably be applied particularly to PCB hot-spots rather than to entire river or lake bottoms. If the PCB and/or other contaminant concentrations were so high as to result in oily fluids oozing from the **sediments**, dredging would be a more appropriate remedy. The geotextile biointrusion barrier could also be used without oxidants underneath as a temporary or even semi-permanent stabilizing measure to contain **sediments** contaminated with lead, methylmercury, radionucleides and/or **PCBs** until a permanent remedy becomes possible.

II. Chemical/Biological Treatment of PCB-Contaminated Sediments

A. ABSTRACT

In the year since we first received grant funding (March 2001) we have completed all of the year 1 objectives related to **chemical treatment** of **PCBs** with **ozone** and CHEMOX®. Those objectives were to test the feasibility of using **ozone** and CHEMOX® (a proprietary oxidant formerly known as BIOX® that comes in powdered form) to oxidize **PCBs** in laboratory experiments, and to determine the **chemical** nature of the oxidation products and their biodegradability. **Ozone** dosage was also determined. In addition, **ozone** tests were done on two polycyclic aromatic hydrocarbons (PAHs).

The two **PCBs** tested were 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB). The first set of tests was conducted with these two **PCBs adsorbed** to kaolinite. Separate reactors were used for DCB and HCB. **Ozone** was bubbled through, and CHEMOX® was manually mixed into the reactors. The concentrations of the two **PCBs**, Cl^-, and **Chemical** Oxygen Demand (COD) were measured over 30 days of contact time with the two oxidants. After 30 days of contact time with the oxidants, the remaining liquid was separated from the kaolinite and placed in bioreactors containing inoculum from the local wastewater **treatment** plant and nutrients and allowed to reactor for 20 days. Table 1 summarizes the results. In addition, **ozone** tests were done on two polycyclic aromatic hydrocarbons (PAHs).

Table 1. Summary of results for 30 days of treatment of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite with ozone and CHEMOX®, followed by 20 days of biodegradation.

Parameter	Ozone	CHEMOX®
Dichlorobiphenyl (DCB)		
DCB Removed with Oxidants (%)	97 ± 4 (9)[a]	99 ± 4 (9)
Cl^- Released with Oxidants (%)	95 ± 3 (9)	97 ± 5 (9)
Cl^- Released/DCB Removed (mol/mol)	1.9 ± 0.5 (43)	2.1 ± 0.7 (38)
Oxidant Dose (g oxidant/g DCB removed)	18.6 ± 2.7 (43)	NM[b]
COD Removed by Biodegradation (%)	92 ± 5 (9)	97 ± 4 (9)
Hexachlorobiphenyl (HCB)		
HCB Removed with Oxidants (%)	92 ± 6 (9)	95 ± 5 (9)
Cl^- Released with Oxidants (%)	93 ± 4 (9)	96 ± 7 (9)
Cl^- Released/HCB Removed (mol/mol)	6.2 ± 0.9 (43)	6.1 ± 0.7 (43)
Oxidant Dose (g oxidant/g HCB removed)	30.0 ± 3.9 (43)	NM
COD Removed by Biodegradation (%)	91 ± 4 (9)	98 ± 3 (9)

[a] average ± standard deviation (number of measurements).

[b] NM=not measured, because the reactants in CHEMOX® are proprietary.

Treatment with **ozone** and CHEMOX® resulted in greater than 90% removal of both **PCBs**. Removal rates were somewhat greater with CHEMOX® than with **ozone**, and were greater for DCB than for HCB. The percent of Cl^- released with the oxidants was nearly identical (considering statistical variation) to the percent removal of the **PCBs**. Moreover, the molar ratio of Cl^- released to DCB and HCB removed was approximately equal to the number of moles of Cl on the respective **PCBs** (i.e., 2 chlorine/mole DCB, and 6 chlorine/mole HCB). These results indicate that chlorine removal was stoichiometric and complete. The major oxidation products were the same for both oxidants-benzoic acids, formate, and oxylate. The results suggest that Cl atoms on the **PCBs** were replaced with OH groups. The **ozone** dose was approximately 19 g and 30 g per g of DCB and HCB, respectively. Dose was not measured for CHEMOX® because there was no way to measure reactant concentrations, as they are proprietary. Microbes from the wastewater **treatment** plant were able to degrade in excess of 90% of the remaining COD from **treatment** with **ozone** and CHEMOX®, though values were higher for CHEMOX®. Similar results were obtained for ozonation followed by biodegradation of the two PAHs tested.

The effect of humic substances, or native organic matter (NOM), on the dose of **ozone** required to oxidize DCB and HCB was tested in separate laboratory experiments. DCB and HCB were allowed to sorb to fine-grained river **sediments** containing approximately 3% by weight of NOM. These **sediments** were then subjected to the same **ozone treatment** tests as the kaolinite slurries. The doses increased substantially relative to kaolinite. **Ozone** doses in the presence of 3% NOM were approximately 237 g/g DCB and 404 g/g HCB. These doses are approximately 13 times greater than those observed in kaolinite. In addition, approximately 55 days were required to reach the same final DCB and HCB concentrations as were obtained after only 30 days with kaolinite. The increase in oxidant dose would likely be similar for CHEMOX®, though these tests could not be conducted because the oxidant is proprietary.

B. MATERIALS AND METHODS

The goal of this part of the research was to test the feasibility of **ozone** and CHEMOX® as a **chemical treatment** to oxidize **PCBs**, and to characterize the oxidation products and their potential to be biodegraded by common environmental microorganisms. Two **PCBs** were used, 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB). Initial tests with **Ozone** and CHEMOX® were done with DCB and HCB **adsorbed** to kaolinite (i.e., without native organic material, or NOM). Similar ozonation studies were also conducted with polycyclic aromatic hydrocarbons (PAHs), because these compounds are also PBTs and are very typical contaminants of **sediments** in Michigan waterways. In addition, more information is available on ozonation of PAHs than **PCBs**, so conducting side-by-side experiments on both PBTs allows a direct comparison to be made between the results from our PBT ozonation studies and those in the literature. The two PAHs tested were anthracene (a 3-ring PAH) and fluoranthene (a 4-ring PAH). Finally, ozonation studies were conducted with DCB and HCB **adsorbed** to river **sediments** having a NOM content of approximately 3%. This experiment was conducted to compare with results from the kaolinite studies in order to determine the affect of NOM on the dose of **ozone** required to oxidize **PCBs**.

Individual slurries were maintained for each PCB and PAH. All four PBTs were added to achieve an initial concentration in the slurry of 1 g/kg. A phosphate buffer was added to maintain a pH of 7 for the **ozone** experiments and 8 for CHEMOX® experiments, which is a pH range commonly found in **sediments** in the Kalamazoo River. After dosing, the slurries were allowed 4 months of contact time before beginning the ozonation experiments to allow sorption of the **PCBs** to the solids. The slurries were then allowed to settle overnight. The liquid was carefully decanted and 1 L of thickened slurry was placed in 1.5 L glass columns with fritted-glass openings at the bottom to allow gas to be sparged upward through the sediment. The solids content of the thickened slurries was approximately 1.8 kg kaolinite/L and 1.5 kg river sediment/L. The **ozone** reactors were sparged with **ozone** using a laboratory **ozone** generator (OL-100, **Ozone** Services, Burton, British Columbia). The **ozone** generator provided known and fixed O_3 concentrations in the influent gas stream. An on-line O_3 monitor was used to measure **ozone** concentrations exiting the reactor. Effluent air was passed through an activated carbon trap to quantify volatile losses of organic material. Two different O_3 concentrations were tested, 0.5% and 5%, to investigate how **ozone** concentration affected rates of oxidation. Control reactors were sparged with laboratory air. Sparging provided the only mixing, in order to simulate conditions encountered with *in situ* sediment sparging.

For CHEMOX® tests, CHEMOX® was placed in the slurry at a mass ratio of 1:10 (CHEMOX® /soil). The CHEMOX® was mixed into the slurry by sparging with nitrogen gas for an hour every 5 days. CHEMOX® control reactors received no CHEMOX®. Additional control reactors for both oxidants were maintained with kaolinite that did not contain added DCB or HCB, to determine the reaction of the oxidants with kaolinite alone. Each reactor type was run in triplicate. The experiments were conducted at approximately 20°C, at which temperature one mole of gas occupies 24.2 L.

During 30 days of reaction, 5 mL slurry samples were extracted with petroleum ether to measure the parent PBT concentrations. PCB concentrations were then determined using gas chromatography (Hewlett-Packard 5890) with electron capture detection (GC/ECD) and PAHs were quantified using GC (Perkin-Elmer Sigma 300) with flame ionization detection (GC/FID). GC/mass spectroscopy (GC/MS) (Hewlett-Packard 5985B MS) was used to tentatively identify oxidation products of the **PCBs** from **treatment** with **ozone** and CHEMOX®. Identification of oxidation products was not done for the PAHs. The liquid fraction of the slurry (5 mL samples) were analyzed for **Chemical** Oxygen Demand (COD) using the Hach COD test and a Hach DR-4000 spectrophotometer. Chlorine (Cl^-) concentration was also measured (with a Dionex IC) in the reactors containing **PCBs** to quantify the release of chlorine atoms during ozonation.

After 30 days of **ozone treatment**, the reactor liquid was separated from the solids using a centrifuge. Approximately 200 mL of liquid was placed in closed, 500 mL glass BOD bottles with 20 mL of inoculum from the Hamilton, Ontario municipal wastewater **treatment** plant. Nitrogen (NH_4Cl) was added as a nutrient. Phosphorus was already present in the liquid because it was used to buffer the pH in the reactors at 8. Triplicates were run of each reactor. Control reactors received no nitrogen. Oxygen consumption was measured and samples were taken periodically to measure COD. The pH in the bioreactors remained at approximately 8.0-8.2 throughout the entire 20 days of **treatment**.

B.1 Materials

Organic chemicals were obtained from Aldrich (Milwaukee, Wisconsin), including the two **PCBs** 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB), the ozonation products 2-hydroxybenzoic and 2,3,4-trihydroxybenzoic acids and formic and oxalic acids, the extractant diethylether, the extraction surrogate 2-fluorobiphenyl, the derivatizing agent diazomethane, and CH_2Cl_2. Table 1 lists important physical properties of DCB and HCB. Kaolinite, NH_4Cl, K_2HPO_4, KH_2PO_4, HCl, and Na_2SO_4 were from Fisher Scientific (Chicago, Illinois). River sediment was from the Grand River at Brantford, Ontario-Canada. Inoculum was from the aeration tank at the domestic wastewater **treatment** plant in Hamilton, Ontario-Canada.

B.2 Sediment and Slurry Preparation

The river sediment was tested for NOM content and particle size distribution according to *Methods of Soil Analysis*.[20] The river sediment was allowed to settle and the excess water was removed. In 50 L Nalgene® carboys, de-ionized water was used to make separate slurries of kaolinite and river sediment with a solids concentration of approximately 80% on a mass basis. The slurries were buffered at a pH of 7 with equal molar ratios of K_2HPO_4 and KH_2PO_4. The slurries were spiked with DCB and HCB to levels of 1000 mg kg^{-1} and were allowed 4 months with daily agitation of the carboys to provide sufficient time for adsorption of the **PCBs** to the solids. Slurries were thickened by allowing the solids to settle for one week and carefully decanting the liquid. The solids concentrations of the thickened slurries were approximately 1800 kg m^{-3} for kaolinite and 1500 kg m^{-3} for river sediment (i.e., mass of dry solids per volume of slurry). The thickened slurries were then used in the sparging reactors.

B.3 Sparging Reactors

The sparging reactors consisted of 1.5 L glass columns with fritted-glass openings at the bottom to allow gas sparging

upward through the sediment. Each reactor contained 1 dm^{-3} of thickened slurry. Triplicate control reactors were sparged continuously with laboratory air. Triplicate **ozone** reactors were sparged continuously with a laboratory **ozone** generator (**Ozone** Services Model OL-100, Burton, British Columbia, Canada), supplying **ozone** at a fixed concentration of 0.5% (v/v). The gas flow rate in all reactors was 50 cm^3 d^{-1}. Effluent **ozone** concentrations were measured daily with a photometer (Anseros Ozonomat GP, Tübingen, Germany). The daily mass of **ozone** consumed in the reactor was quantified as the difference between the known influent the average effluent concentrations. Effluent gas was passed through activated carbon to quantify stripping of DCB and HCB. The reactors were maintained at 20°C.

The reactors containing kaolinite and river sediment were sparged for 30 days and 55 days, respectively. Periodically 20 cm^3 slurry samples were taken, reactor contents were gently mixed, and pH was measured with a probe. The volume of water lost through evaporation was replaced after each sampling event. Slurry samples were centrifuged for 10 min at 10,000 rpm. The supernatant was filtered (0.45 μm) and soluble **chemical** oxygen demand (COD) and Cl^- were analyzed in quadruplicate sub-samples. The soil pellet was placed under suction on a 0.45 μm filter to remove as much water as possible. The moisture content was then determined on 3 to 4 g samples according to *Methods of Soil Analysis*.[20] Anhydrous Na_2S0_4 was added to absorb remaining water. Quadruplicate sub-samples were taken for extraction and analysis of **PCBs**. Activated carbon was prepared in the same way. After sparging a 30 cm^3 sample was centrifuged and filtered to characterize oxidation products that had accumulated in the aqueous phase.

B.4 Bioreactors

After 30 days of **ozone** sparging, the remaining contents from each reactor (approximately 650 cm^3) were separated from the solids by centrifuging. The liquid fraction (approximately 200 cm^3) was placed in closed, 500 cm^3 glass bottles with 20 cm^3 of inoculum. The biomass concentration of the inoculum was measured using *Standard Method* 2540-D.[21] Nitrogen was added as NH_4Cl, at a mass ratio of 4 g N per g of COD. Phosphorus was added as equal molar ratios of K_2HPO_4 and KH_2PO_4 (0.4 g P per g COD) as a nutrient and to buffer at pH 7. Nutrients and inoculum were added to liquid from two of the three **ozone**-sparged reactors, and the third (a control) received no amendments. The bottles were attached to a Hach BODTrak® to monitor O_2 consumption. Periodically, pH was measured with a probe and 10 cm^3 samples were taken and filtered (0.45 μm) to measure COD. The bioreactors were maintained for 20 days.

B.5 Analytical Methods

DCB and HCB were quantified in quadruplicate 3 to 4 g samples of prepared sediment and activated carbon. **PCBs** were extracted from the samples by adding 10 cm^3 of diethylether and shaking intensely for 1 hour. 2-fluorobiphenyl dissolved in diethylether (0.5 cm^3 of a 2000 g m^{-3} solution) was added as an extraction surrogate. DCB and HCB were quantified using gas chromatography (GC) with electron capture detection (ECD). Two mm^3 of diethylether extract were injected in a Hewlett-Packard 5890 GC with a DB-5 column from J&W Scientific (30 m x 0.32 mm). The injector temperature was 265°C. He flow was 1 cm^3 min^{-1}. The temperature profile was 2 min at 100°C, 8°C min^{-1} to 270°C, 3 min holding, and 24°C min^{-1} to 300°C, 10 min hold. Recovery of 2-fluorobiphenyl was in excess of 95%. Maximum rates of disappearance of DCB and HCB were measured with linear regression analysis.

GC/mass spectroscopy (GC/MS) was used to identify products of PCB reaction with **ozone** and CHEMOX® in duplicate 10 cm^3 filtrate samples from the reactors. The samples were first acidified to a pH of 2 with HCl. The water was extracted three times with CH_2Cl_2. The aqueous layer was discarded and the CH_2Cl_2 was reduced to a volume of 4 cm^3 under a gentle N_2 gas stream. The reduced samples were derivatized with diazomethane and then reduced to 4 mm^3. Solutions (1 molar) of 2-hydroxybenzoic acid and 2,3,4-trihydroxybenzoic acid, formic acid, and oxalic acid were made with de-ionized water and prepared in the same way. Injections (2 mm^3) were done in splitless mode on a

Hewlett-Packard 5890 GC with the column described above. The temperature profile was 30°C to 170°C at 3°C min^{-1}, 10°C min^{-1} to 250°C, and 20°C min^{-1} to 290°C with a 20 min hold. The MS was a Hewlett-Packard 5973 operated in the electron impact mode and scanned between m/z 40 and m/z 250.

Cl^- concentrations were measured in quadruplicate filtrate samples using a Dionex ion chromatograph (IC). A Dionex Ion Pac As11 column (4 mm diameter) was used, followed by a Dionex anion self-regenerating membrane suppressor. With a liquid flow rate of 1.2 cm^3 min^{-1}, the gradient used mixtures of de-ionized water and 2000 g m^{-3} NaOH at the following ratios of water/NaOH: 3 min at 98/2, 5 min at 40/60, 9 min at 0/100, 5 min at 98/2. Soluble COD was measured in quadruplicate 2 cm^3 filtrate samples according to *Standard Method* 5220-D[21], using the Hach COD test (2 g m^{-3} quantification limit) and a Hach DR/4000 Spectrophotometer.

C. RESULTS AND DISCUSSION

C.1 Chemical/Biological Treatment of PBTs

C.1.1 OZONE TREATMENT OF PCBs

The time profiles of the concentration of DCB and HCB in the reactors sparged with **ozone** are shown in Figure 1. The control reactors sparged with air maintained the initial DCB and HCB concentrations of 1000 mg/kg and showed essentially no removal of either PCB over the 30 day period. In contrast, the reactors sparged with **ozone** showed a considerable decrease in concentration of both DCB and HCB. The final concentration, after 30 days, of DCB and HCB were approximately 30 mg/kg and 60 mg/kg, respectively. Sparging with air (in the controls) or **ozone** at a concentration of 0.5% would cause essentially the same stripping of DCB and HCB. Furthermore, DCB and HCB are highly non-volatile. Since no measurable stripping occurred with air sparging, it can be concluded that the reduction in PCB concentrations was the result of reaction with **ozone**. This conclusion is supported by a decrease in **ozone** concentration measured across the reactors (data not shown), which shows that **ozone** was being removed via reaction. Control reactors containing kaolinite with no added DCB or HCB showed essentially no reaction with **ozone**, further indicating that **ozone** reacted with the **PCBs**. Hence, it can be concluded that the loss of DCB and HCB shown in Figure 1 was due to reaction with **ozone**.

Figure 2 shows the production of COD dissolved organic carbon in the reactors during sparging with **ozone**. COD is a measure of the dissolved organic carbon present in the liquid. The COD value of the original slurry was zero, because DCB and HCB are sparingly soluble and remain sorbed to the kaolinite. An increase in COD represents a conversion of the **PCBs** to soluble organic compounds. COD values in the control reactors sparged with air remained at zero throughout the study period. However, COD accumulated in the reactors sparged with **ozone**. Maximum values occurred between 14 days and 18 days. After this time, COD values began to decrease, which can be explained by further oxidation of the initial oxidation products via reaction with **ozone**. Samples of liquid from the reactors were taken after day 30 to identify the ozonation products with GC/MS. The results showed that the predominant compounds comprising the COD were hydroxylated benzoic acids, oxylate, formate, and acetate. These products are known to be biodegradable. No chlorinated compounds were identified in the liquid. The presence of hydroxyl groups on the benzoic acids indicates that reaction with **ozone** replaced Cl atoms on the **PCBs** with OH. Ring cleavage also must have occurred to form the organic acid products identified with GC/MS. Results from other investigations treating chlorinated organics with **ozone** or other oxidants that produce hydroxyl free radicals (e.g., Fenton's Reagent) show that the C-Cl bonds are labile, and that Cl is readily replaced with hydroxyl groups (Heinzle et al., 1995). The accumulation of COD in the **ozone**-sparged reactors indicates that the oxidation products were not nearly as susceptible to attack by **ozone** as were the original **PCBs**.

Figure 3 shows the concentration of chloride ion (Cl^-) in the reactors during **ozone** sparging. The control reactors maintained a Cl^- concentration of zero throughout the 30 days. Control reactors containing kaolinite but no PCB (data not shown) had zero Cl^- concentrations throughout the period, as would be expected. In contrast, the Cl^- concentration in the **ozone**-sparged reactors increased steadily throughout the study period. These results, when considered with those shown in Figures 1 and 2, show that Cl^- was released from DCB and HCB during **treatment** with **ozone**. The GC/MS

results indicate that Cl^- atoms were replaced with OH groups, as discussed above. These results also suggest that measuring the Cl^- concentration in future studies could be used as a surrogate measure of removal of **PCBs** by reaction with **ozone**.

The change in COD concentrations with time in the bioreactors treating **PCBs** already reacted with **ozone** is shown in Figure 4. The initial concentrations of COD in the bioreactors are similar to the final COD concentrations in the **ozone**-sparged reactors (see Figure 2). Slight dilution did occur from addition of inoculum from the wastewater **treatment** plant and nitrogen (approximately 30 mL added to 300 mL of effluent from the **ozone**-sparged reactors). Control reactors received no nitrogen, and these reactors showed no decrease in COD with time. Nor did the control reactors show significant uptake of oxygen (data not shown) except for that exerted by endogenous respiration of the microorganisms present in the inoculum. The active reactors (with added nitrogen) showed a considerable decrease in COD with time. Since the bottles were closed, stripping could not be a mechanism for COD reduction in the active bioreactors. Moreover, oxygen uptake (data not shown) was high in the active reactors, and decreased sharply on day 16 when the COD removal decreased. These results support the conclusion that products of PCB reaction with **ozone** are readily degradable under aerobic conditions. These results are consistent with those of Aronstein and Rice (1995) and Carberry and Yang (1994) who reported that products of oxidation of **PCBs** with Fenton's Reagent are readily biodegradable.

Figure 1. Removal of DCB and HCB resulting from ozone sparging.

Figure 2. Production of COD during ozone sparging of DCB and HCB.

Figure 3. Chloride ion release during ozone sparging of DCB and HCB.

Figure 4. COD removal in bioreactors treating oxidation products of DCB and HCB from reaction with ozone.

The results from the ozonation and biodegradation of DCB and HCB are summarized in Table 2. The removal of DCB was 97% after 30 days, compared with 92% for HCB. The lower removal of HCB may be due to its lower aqueous solubility than DCB. The concentration of O_3 in the reactors had no impact on the removal of DCB and HCB, indicating that rates of reaction with O_3 were limited by desorption of **PCBs** from the kaolinite. Removal of approximately 2 and 6 chlorine atoms from dichlorobiphenyl and hexachlorobiphenyl, respectively, shows that chlorine atoms were stoichiometrically (i.e., completely) removed from the **PCBs** during ozonation. Close agreement between percent removal of the two **PCBs** and percent Cl^- released also indicates stoichiometric removal of chlorine atoms from the **PCBs** by **ozone**. These results suggest that ozonation replaced chlorine atoms in the **PCBs** with hydroxyl (OH) groups, and that ring cleavage also occurs. The **ozone** dose was approximately 19 g and 30 g per g of DCB and HCB, respectively. COD reduction in the bioreactors was in excess of 90%, which shows that the ozonation products of DCB and HCB are readily biodegradable. Furthermore, COD accumulated during ozonation (see Figure 2), which indicates that the partial oxidation products were not nearly as susceptible to attack by **ozone** as were the original **PCBs**.

Table 2. Summary of results for 30 days of ozone sparging of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite, followed by 20 days of biodegradation.

Dichlorobiphenyl (DCB)	
DCB Removed with **Ozone** (%)	97 ± 4 (9)[a]
Cl^- Released with **Ozone** (%)	95 ± 3 (9)
Cl^- Released/DCB Removed (mol/mol)	1.9 ± 0.5 (43)
Ozone Dose (g **ozone**/g DCB removed)	18.6 ± 2.7 (43)
COD Removed by Biodegradation (%)	92 ± 5 (9)
Hexachlorobiphenyl (HCB)	
HCB Removed with **Ozone** (%)	92 ± 6 (9)
Cl^- Released with **Ozone** (%)	93 ± 4 (9)
Cl^- Released/HCB Removed (mol/mol)	6.2 ± 0.9 (43)
Ozone Dose (g **ozone**/g HCB removed)	30.0 ± 3.9 (43)
COD Removed by Biodegradation (%)	91 ± 4 (9)

[a] average ± standard deviation (number of measurements).

Aronstein and Rice (1995) obtained similar results using Fenton's reagent to treat **PCBs**. In this study, Fenton's reagent increased the overall amount of **PCBs** degraded by 4 times relative to sediment samples not treated with Fenton's reagent. Their study also showed that the partial oxidation products were highly soluble compared with the parent **PCBs**. This study showed that chlorine atoms on the **PCBs** were replaced by hydroxyl groups during ozonation. Heinzle et al. (1995) also observed stoichiometric chlorine replacement with OH groups during ozonation of chloroguaiacols (i.e., chlorinated methoxy phenols). Heinzle et al (1995) also observed ring cleavage, and a 10-fold increase in biodegradation of the partial oxidation products compared with the original chloroguaiacols. The stoichiometric replacement of chlorine with hydroxyl groups means that **ozone** dose increases with increasing degree of chlorination on the **PCBs** (Table 1). The fact that hexachlorobiphenyl used approximately three times more **ozone** than dichlorobiphenyl, and that the molar ratio of O_3 consumed/PCB consumed was also about 3 times greater for HCB than DCB suggests that **ozone** is used to achieve complete dechlorination. Heavily chlorinated **PCBs** would then exert a high **ozone** demand. Marvin et al. (1998) reported preferential oxidation of chlorinated compounds (pentachlorophenol) to non-chlorinated organics (PAHs) with **ozone**. Non-chlorinated organic wastes exert **ozone** demands ranging from approximately 4-5 g O_3/g COD (Narkis and Schneider-Rotel, 1980; Jones et al., 1985). The identification of hydroxylated benzoates in the residual COD in these studies is also consistent with advanced oxidation of **PCBs** reported by Brubaker and Hites (1998). These results clearly indicate that **treatment** with **ozone** and CHEMOX® are consistent with those of Aronstein and Rice (1995) and Carberry and Yang (1994) who reported that products of oxidation of **PCBs** with Fenton's Reagent are readily biodegradable.

C.1.2 EFFECT OF NOM ON **OZONE TREATMENT** OF **PCBs**

The effect of the presence of NOM on the **ozone** dose required to achieve oxidation of **PCBs** in **sediments** was determined by measuring DCB and HCB concentrations with time in the river **sediments** having a 3% NOM content. The concentrations of DCB and HCB were measured with time in an **ozone**-sparged reactor, as well as the difference in **ozone** concentration across the reactors. The **ozone** doses required to achieve PCB removal in the river **sediments** similar to those observed in kaolinite were 237 g/g DCB and 404 g/g HCB. These doses are approximately 13 times greater than those observed in kaolinite. The results also showed that approximately 55 days of **ozone** sparging were

required in the river **sediments** to achieve the same removal of DCB and HCB that were obtained in kaolinite slurries in 30 days. It is known that NOM scavenges oxidants of any kind (i.e., Fenton's Reagent, hydrogen peroxide, permanganate, etc.). NOM is of concern because it increases the required dose of oxidant and the time required to achieve a given cleanup level, and therefore increases the cost of remediation.

C.1.3 **OZONE TREATMENT** OF PAHs

The results from the ozonation and biodegradation of anthracene (a 3-ring PAH, MW=178) and fluoranthene (a 4-ring PAH, MW=230) are summarized in Table 3. The removal of anthracene and fluoranthene by **ozone treatment** was 99% and 94%, respectively. The slightly lower removal of fluoranthene may have been a result of its lower aqueous solubility. The mass ratio of O_3 consumed/PAH removed was slightly higher for fluoranthene (6.4) than for anthracene (7.1). These values are consistent with those reported for ozonation of oil shale wastewaters (Jones et al., 1985; Clayton, 1998). In excess of 95% of the residual COD from **ozone treatment** of both PAHs was biodegraded under aerobic conditions. These results are similar to those obtained by several other studies (Brown et al., 1997; Nelson et al., 1997; Marvin et al., 1998). Ozonation products were not identified for the PAHs. Fluoranthene removal was less that that observed for anthracene. Using a higher **ozone** concentration during sparging had no measurable effect on rate and extent of removal of either PAH, which suggests that the rate of desorption from the kaolinite limited the rate of removal via ozonation. This may be due to the greater hydrophobicity of fluoranthene, which gives it a greater tendency to sorb to the solids than anthracene. This trend was also observed for the two **PCBs** tested.

Table 3. Summary of results for 30 days of ozone sparging of anthracene and fluoranthene, followed by 20 days of biodegradation.

Anthracene	
Anthracene Removed by **Ozone** (%)	99 ± 1 (3)[a]
Ozone Dose (g **Ozone**/g Anthracene Removed)	6.4 ± 0.5 (3)
COD Removed by Biodegradation (%)	96 ± 6 (3)
Fluoranthene	
Fluoranthene Removed by **Ozone** (%)	94 ± 7 (3)
Ozone Dose (g **Ozone**/g Fluoranthene Removed)	7.1 ± 0.4 (3)
COD Removed by Biodegradation (%)	98 ± 5 (3)

[a] average ± standard deviation (number of measurements).

C.1.2 CHEMOX®

The results for CHEMOX® were generally very similar to those obtained with **ozone**. The time profiles of the concentration of DCB and HCB in the reactors treated with CHEMOX® are shown in Figure 5. The control reactors sparged without CHEMOX® maintained the initial DCB and HCB concentrations of 1000 mg/kg to 1100 mg/kg and showed essentially no removal of either PCB over the 30 day period. In contrast, the reactors with CHEMOX® showed a considerable decrease in concentration of both DCB and HCB. The final concentrations of DCB and HCB were both below 100 mg/kg. DCB and HCB are highly non-volatile, and no measurable stripping occurred with nitrogen sparging. Hence, it can be concluded that the reduction in PCB concentrations was the result of reaction with CHEMOX®. This conclusion cannot be supported by a decrease in concentration of the reactants, because CHEMOX® is a proprietary product.

Figure 6 shows the production of COD dissolved organic carbon in the reactors during reaction with CHEMOX®. The COD value of the original slurry was zero, because DCB and HCB are sparingly soluble and remain sorbed to the kaolinite. An increase in COD represents a conversion of the **PCBs** to soluble organic compounds. COD values in the control reactors without CHEMOX® remained at zero throughout the study period. However, COD accumulated in the reactors treated with CHEMOX®. Maximum values occurred between 14 days and 20 days. After this time, COD values began to decrease, which can be explained by further oxidation of the initial oxidation products via reaction with CHEMOX®. Samples of liquid from the reactors were taken after day 30 to identify the oxidation products with GC/MS. The results showed that the predominant compounds comprising the COD were hydroxylated benzoic acids, oxylate, formate, and acetate. These products are the same as those obtained with **ozone treatment**, and are known to be biodegradable. No chlorinated compounds were identified in the liquid. The presence of hydroxyl groups on the benzoic acids indicates that reaction with CHEMOX® replaced Cl atoms on the **PCBs** with OH. Ring cleavage also must have occurred to form the organic acid products identified with GC/MS. Results from other investigations treating chlorinated organics with oxidants that produce hydroxyl free radicals (e.g., Fenton's Reagent) show that the C-Cl bonds are labile, and that Cl is readily replaced with hydroxyl groups (Heinzle et al., 1995). The accumulation of COD in the reactors containing CHEMOX® indicates that the oxidation products were not nearly as susceptible to attack by **ozone** as were the original **PCBs**. The final COD values after **treatment** with CHEMOX® 30 days were approximately 1000 mg/L greater than those observed with **ozone treatment** (cf. Figures 2 and 6).

Figure 7 shows the concentration of chloride ion (Cl^-) in the reactors during **treatment** with CHEMOX®. The control reactors maintained a Cl^- concentration of zero throughout the 30 days. In contrast, the Cl^- concentration in the CHEMOX®-treated reactors increased steadily throughout the study period. These results, along with those shown in Figures 5 and 6, show that Cl^- was released from DCB and HCB during **treatment** with CHEMOX®. The GC/MS results also indicate that Cl^- atoms were replaced with OH groups. These results also suggest that measuring the Cl^- concentration in future studies could be used as a surrogate measure of removal of **PCBs** by reaction with oxidants such as **ozone** and CHEMOX®.

The change in COD concentrations with time in the bioreactors treating **PCBs** already reacted with CHEMOX® is shown in Figure 8. The initial concentrations of COD in the bioreactors are similar to the final COD concentrations in the CHEMOX®-treated reactors (see Figure 6). Slight dilution did occur from addition of inoculum from the wastewater **treatment** plant and nitrogen (approximately 30 mL added to 300 mL of effluent from the CHEMOX®-treated reactors). Control reactors received no nitrogen, and these reactors showed no decrease in COD with time. Nor did the control reactors show significant uptake of oxygen (data not shown) except for that exerted by endogenous respiration of the microorganisms present in the inoculum. The active reactors (with added nitrogen) showed a considerable decrease in COD with time. Since the bottles were closed, stripping could not be a mechanism for COD reduction in the active bioreactors. Moreover, oxygen uptake (data not shown) was high in the active reactors, and decreased sharply on day 16 when COD removal decreased. These results support the conclusion that products of PCB reaction with CHEMOX® are readily biodegradable under aerobic conditions.

Figure 5. Removal of DCB and HCB resulting from CHEMOX®-treatment.

Figure 6. Production of COD during CHEMOX®-treatment of DCB and HCB.

Figure 7. Chloride ion release during CHEMOX®-treatment of DCB and HCB.

Figure 8. COD removal in bioreactors treating oxidation products of DCB and HCB from reaction with CHEMOX®.

The results from the CHEMOX® **treatment** and biodegradation of DCB and HCB are summarized in Table 4. The removal of DCB was 99% after 30 days, compared with 95% for HCB. The lower removal of HCB may be due to its lower aqueous solubility than DCB. Removal of nearly 2 and 6 chlorine atoms from dichlorobiphenyl and hexachlorobiphenyl, respectively, shows that chlorine atoms were stoichiometrically (i.e., completely) removed from the **PCBs** during CHEMOX® **treatment**. Close agreement between percent removal of the two **PCBs** and percent Cl^- released also indicates stoichiometric removal of chlorine atoms from the **PCBs** by CHEMOX®. These results suggest that CHEMOX® replaced chlorine atoms in the **PCBs** with hydroxyl (OH) groups, and that ring cleavage also occurs. COD reduction in the bioreactors was in excess of 97% for both **PCBs**, which shows that the products of reaction of DCB and HCB are readily biodegradable. Furthermore, COD accumulated during CHEMOX® **treatment** (see Figure 6), which indicates that the partial oxidation products were not as susceptible to attack by CHEMOX® as were the original **PCBs**.

Table 4. Summary of results for 30 days of CHEMOX® treatment of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite, followed by 20 days of biodegradation.

Dichlorobiphenyl (DCB)	
DCB Removed with CHEMOX® (%)	99 ± 4 (9)
Cl^- Released with CHEMOX® (%)	97 ± 5 (9)
Cl^- Released/DCB Removed (mol/mol)	2.1 ± 0.7 (38)
COD Removed by Biodegradation (%)	97 ± 4 (9)
Hexachlorobiphenyl (HCB)	
HCB Removed with CHEMOX® (%)	95 ± 5 (9)
Cl^- Released with CHEMOX® (%)	96 ± 7 (9)
Cl^- Released/HCB Removed (mol/mol)	6.1 ± 0.7 (43)
COD Removed by Biodegradation (%)	98 ± 3 (9)

[a] average ± standard deviation (number of measurements).

D. SUMMARY

The results from the **chemical treatment** studies clearly show that:

- **treatment** of PBTs with **ozone** and CHEMOX® decreased PBT concentrations in soil,

• stoichiometric removal of chlorine atoms accompanied removal of DCB and HCB by **treatment** with **ozone** and CHEMOX®,

• the residual organic carbon after **treatment** of PBTs with **ozone** and CHEMOX® was readily biodegradable,

• **treatment** of PBTs with **ozone** and CHEMOX® increased the aqueous solubility of the residual organic carbon relative to the parent compounds,

• NOM increases the dose of oxidant required to achieve PBT removal because NOM scavenges both **ozone** and CHEMOX®.

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Native organics

matter produced.

Final Report

for the

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Development of Innovative Remedial Methods for PBT-Contaminated Sediments in the Great Lakes Drainage Basin

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Sediments in the Great Lakes Drainage Basin

Executive Summary

Persistent, Bioaccumulative Toxin (PBT)-contaminated **sediments** pose health risks due to contaminant movement up the food chain to fish and humans. PBTs include lead, mercury, **PCBs**, PAHs and certain other organic contaminants. Our goal was to test a new method to cut off contaminated **sediments** from the food chain.

Our method is to cover "hot spots" in the stream or lake bed with an anchored geotextile layer to stop biointrusion and erosion. The permeable geotextile fabric is covered with sand, gravel and/or cobbles to cut off benthic organisms from feeding in the contaminated **sediments**, and prevent erosion of these **sediments** while allowing groundwater inflow. This method can be **combined** with biochemical methods to hasten contaminant degradation beneath the geotextile.

Two geotextiles used as biointrusion barriers were evaluated in laboratory permeameters containing **sediments**; one of the geotextiles was also evaluated in Gull Creek, Michigan. The field trial included four 3 x 3 meter patches in the creek bed. Two of the patches were covered with a geotextile topped with 1-3 cm of anchoring sand and pea gravel; the other two patches were controls. Six months later one of the controls was sampled, and a geotextile patch was sacrificed to permit sampling underneath.

Results of lab and field trials to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in **sediments**. Only 4.26 ± 2.47% of the organisms present moved through the geotextiles ($t_g = 3.25$, $P < 0.05$) in lab Trials 2-4. In Gull Creek, benthic invertebrate density was reduced by 93.5% under the geotextile-covered patch relative to the control after six months of coverage.

Ozone and CHEMOX® were both successful in greatly speeding up the breakdown of **PCBs** and other persistent contaminants like PAHs in laboratory tests. **Treatment** with **ozone** and CHEMOX® resulted in greater than 90% removal in one month of both **PCBs** tested. The amounts of oxidants required and the time needed for detoxification both increased as the fraction of natural organic matter in the contaminated **sediments** increased. The method also requires spreading the oxidants thoroughly through the contaminated **sediments**. Application of these oxidants will be most successful in **sediments** contaminated with organic chemicals with low proportions of organic matter and into which the oxidants can be disseminated well.

These preliminary tests of this new method for reducing health risks from contaminated **sediments** suggest that the geotextile biointrusion barrier has great promise and should be further evaluated in full-scale field trials. The **chemical** oxidants (especially CHEMOX®) may be **combined** with the geotextile barrier in future field trials, and should be used in separate trials focusing upon detoxification of dredge spoils prior to disposal.

Development of Innovative Remedial Methods for PBT-Contaminated

Sediments in the Great Lakes Drainage Basin

Introduction

Current remedial methods for PCB-contaminated **sediments** in river and lake bottoms and harbors and shores are woefully inadequate. The most frequently chosen remedial method is dredging. Dredging is sometimes effective, particularly in the case of grossly contaminated **sediments**, but has four serious drawbacks. (1) Where and how can we dispose of the dredge spoils? Typical answers are incineration (which creates dioxins) and/or dumping in somebody's

back yard (often in a poor and/or minority community). (2) Additional spreading of contamination and resulting risk to human health and the environment is often induced by disturbing and resuspending the **sediments** during dredging. (3) Dredging never removes all contaminated **sediments** (90% removal would be an optimistic goal in most cases). Thus dredging leaves a source (about 10% of contaminant mass) in place and more exposed due to removal of the overlying **sediments**. (4) Dredging completely disrupts habitat and ecological values of streams and lakes. A relatively new alternative to dredging is subaqueous capping in place, or armored stream or lake bottoms. This "management in place" results in an underwater landfill, a toxic waste site gift-wrapped for future generations to inherit. It is hard to believe that these are the best methods we have developed to deal with contaminated **sediments**.

To develop a better remedial method for contaminated **sediments**, it is first helpful to recognize four basic principles. 1. Streams and lakes are hydrologically active water bodies that connect with and exchange water with groundwater aquifers. Many surface water bodies would dry up without groundwater inflow. Blocking water flow through lake and river **sediments**, such as would occur in subaqueous capping, is not acceptable. 2. **PCBs** and many other persistent contaminants found in **sediments** tend to adsorb strongly to those (primarily fine-grained) **sediments**. To control the contaminants, we must control the **sediments**. Yet the usual fate of sedimentary deposits is further erosion and transport and redeposition. 3. These persistent chemicals degrade slowly if at all. Yet biodegradation in place, if it could be accelerated, would likely be the most feasible solution to this problem of broadly disseminated pollution. 4. These chemicals adsorb not only to fine-grained **sediments**, but often to the fatty tissue of biota. Many organisms contact and adsorb these contaminants as they burrow through or stir up **sediments** looking for food. At higher levels of the food chain, the contaminants they adsorb may be biomagnified and represent a threat to human health as well as the environment.

We propose a new method for managing in place **sediments** contaminated with PBTs, including **PCBs**, PAHs, lead and mercury. This method could be called anchored permeable geotextile biointrusion barriers. Briefly, the concept is that the contaminated **sediments** should be managed in place using a permeable geotextile layer to prevent biointrusion by benthic organisms or sediment-mining fish. This biointrusion barrier is held in place, or "anchored", against erosion by water currents using sand, gravel and/or cobbles as required by the currents. There are many different geotextiles, some of which have been developed to stabilize stream banks against erosion, others for draining leachate from underneath landfills. The specific geotextile fabric chosen, and the thickness and grain size of the anchoring layers would be determined on a site-specific basis, taking into account the size of the predominant benthic organisms to exclude from beneath the geotextile barrier and the water currents to be overcome.

The anchored permeable geotextile biointrusion barrier would be an improvement over the subaqueous capping in place method because it allows water to continue to feed the surface water body. It would also allow biodegradation of organic contaminants such as **PCBs** and PAHs to slowly continue, in contrast to a subaqueous cap which would cut off **sediments** from the surroundings and also likely terminate biodegradation. Nevertheless, an approach relying upon natural biodegradation of **PCBs** would not remove the contaminant mass at an adequate rate to satisfy most host communities.

An important addition to the anchored permeable geotextile biointrusion barrier would be a method to accelerate the rate of PCB biomineralization. If such a method could be deployed along with the biointrusion barrier, then the investment of our society's resources in emplacing the biointrusion barrier could be justified because it would eventually result in contaminant removal from the biosphere. This would be a method of remediating contaminated **sediments** worthy of research and development.

We propose that the rate of PCB biomineralization may be enhanced by the addition of **ozone** or by a proprietary oxidant, CHEMOX®. **Ozone** can work at neutral pH to chemically dechlorinate many chlorinated organics. The breakdown products of PCB congener dechlorination may be more biodegradable. Hence, we proposed first conducting a laboratory study to test the merits of this idea. If the lab tests are promising, we wish to study this idea in concert with our biointrusion barrier to see if, together, they could provide a reasonable solution for remediating some PCB-contaminated **sediments** in lakes and rivers.

Of course, no remedial method will solve all problems. Usually several remedial methods are used in concert to deal with real-world problems. It is likely that this proposed method would be most applicable to exposed and/or shallow

sediments near shore that are vulnerable to erosion. It would probably be applied particularly to PCB hot-spots rather than to entire river or lake bottoms. If the PCB and/or other contaminant concentrations were so high as to result in oily fluids oozing from the **sediments**, dredging would be a more appropriate remedy. The geotextile biointrusion barrier could also be used without oxidants underneath as a temporary or even semi-permanent stabilizing measure to contain **sediments** contaminated with lead, methylmercury, radionucleides and/or **PCBs** until a permanent remedy becomes possible.

This study was conducted in two separate parts. One research effort focused on the feasibility of geotextiles as biointrusion barriers. The other effort examined the efficacy of **chemical** oxidants for accelerating PCB degradation in contaminated **sediments**. These two efforts are reported separately below, each with its own abstract.

I. Using Geotextile Biointrusion Barriers to Remediate Contaminated Sediments

A. ABSTRACT

Contaminated river, lake and harbor **sediments** are one of the more challenging remedial legacies we must face in order to reduce risk to human health and the environment. In most locations, these risks are entirely due to contaminant movement from these **sediments** up the food chain to fish and their predators, including humans. Common contaminants include mercury, lead, **PCBs** and other organic chemicals that adsorb to fine **sediments** and the organic materials they contain. The goal of this study was to devise and test an in-situ method to stabilize the contaminated **sediments** and cut them off from the food chain.

The method we propose is to place an anchored geotextile layer over hot spots in the stream or lake bed to serve as a barrier to biointrusion and erosion. A geotextile is a permeable fabric used on or within soils that is made of plastic fibers selected for durability, strength and other design objectives. The geotextile fabric is covered with enough sand, gravel and/or cobbles to hold it in place on top of contaminated **sediments**. The geotextile plus anchoring granular layer prevents erosion and remobilization of the contaminated **sediments**, cuts off benthic organisms and demersal fish from living and feeding in the contaminated **sediments**, and holds the **sediments** in place while allowing groundwater to continue feeding the stream or lake. The biointrusion barrier is an alternative to dredging and landfilling the contaminated **sediments**, the most common remedial alternative, and to covering them with an impermeable HDPE liner, another alternative that creates an underwater landfill and cuts off groundwater base flow. It can be **combined** with biochemical methods to hasten contaminant degradation beneath the geotextile, and/or with chemicals that enhance contaminant sorption to the geotextile.

The effectiveness of two geotextiles as a biointrusion barrier was evaluated in laboratory permeameters containing **sediments** from Gull Creek, Michigan; one of the geotextiles was also evaluated in Gull Creek. The lab experiment followed a completely crossed factorial design involving two types of nonwoven geotextile patches, two types of stream **sediments** (sandy vs more organic, finer stream bed **sediments**), and live organisms vs killed controls. Combinations of treatments were randomly assigned to trials and permeameters. The field trial included four 3 x 3 meter patches in the bed of Gull Creek. **Sediments** from each of the patches were sampled to determine density of benthic organisms. Then two of the patches were covered with a geotextile layer topped with 1-3 cm of anchoring sand and pea gravel; the other two patches served as controls. Six months later one of the controls was sampled, and a geotextile patch was sacrificed to permit sampling underneath. The other geotextile patch will be sacrificed in 10/02 and all four patches will be sampled again.

Results of trials conducted to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in Gull Creek **sediments**. After some slight methodological flaws were discovered in Trial 1, only 4.26 ± 2.47% of the individuals present moved through the geotextile ($t_g = 3.25$, $P < 0.05$) in Trials 2-4. All of the animals that moved through the geotextiles in Trials 2-4 were roundworms or oligochaete annelid worms which, in general, have very small cross-sectional areas. The geotextiles were quite effective barriers against the

movement of the remaining infaunal taxa present in the permeameters, including copepods, ostracods, gammarid amphipods, and chironomid larvae. Surprisingly, the thinner geotextile was a better barrier to benthic invertebrates than the heavier, thicker geotextile used in the field test. The field test results to date largely support the laboratory test results. The four patches were initially (10/01) dominated by copepods, amphipods, oligochaetes, and roundworms. After a winter (4/02), the control patch sampled had a lower density consisting primarily of roundworms (31.1%), copepods (28.8%), and oligochaete worms (15.8%). The **sediments** under the geotextile patch contained only roundworms (65.2%) and ostracods (34.8%). Benthic invertebrate density was reduced by 93.5% in the geotextile-covered patch relative to the control after six months of coverage.

These preliminary tests of this new method for reducing health risks from contaminated **sediments** suggest that the geotextile biointrusion barrier has great promise and should be further evaluated in full-scale field trials.

b. compariSON OF different geotextiles for suitablility

Geotextiles are permeable fabrics of plastic fibers used within soil masses to accomplish certain functions: separation, reinforcement, filtration, drainage, and/or containment. Plastic fibers are used because of long life, excellent durability and strength. Particular polymers can be chosen as a fiber source to produce a geotextile ideally suited for a given application. There are currently at least 100 specific application areas for geotextiles. Our research is proposing a new application for geotextiles: to be used on top of contaminated stream sediments as a biointrusion barrier, a stream sediment filter and erosion barrier.

There are two main types of geotextiles: woven and non-woven. Non-woven geotextiles are almost always chosen over woven geotextiles for applications involving filtration because they have smaller and more uniform openings. However, a few people feel that woven geotextiles can perform better in creating graded filters in the long run because they are less prone to clog.

There are hundreds of different geotextiles available from several domestic and foreign manufacturers. To help choose which ones to test, we attended two international meetings in spring 2001. We visited with manufacturers and with many of their customers. These geotextile experts gave us many different recommendations as to which geotextiles to use. However, they did agree that there were a few experts in the use of geotextiles whom we should contact. Tops on everyone's list was John Price of Price & Company in Wyoming, Michigan. John is the elected president of the International Erosion Control Association, one of the two meetings we attended. John provided us with test samples of several of the Amoco geotextiles he supplies to users, primarily non-wovens. We also obtained test samples from several other manufacturers. John told us (as did several other experts) that he had seen geotextiles used to cover contaminated **sediments** in streams and ponds, but neither he nor anyone else we met had ever heard of the idea of using geotextiles to prevent biointrusion into contaminated **sediments**. He suggested several non-wovens that were strong enough and had been successful for him in the past. Therefore, we decided to test those first.

C. MATERIALS AND METHODS

We conducted laboratory tests of various geotextiles. We set up six permeameters containing sediment samples from Gull Creek. These 5-cm thick sediment samples were covered with one of two geotextiles, followed by 2.5-3.0 cm of clean fine white sand. The permeameters were connected with a constant-head water source flowing into the bottom and upward through the **sediments**, the geotextile and overlying anchoring sand layer. The permeameters were placed inside a refrigerator to replicate Michigan field conditions prevalent at the time of sediment sampling. Our goals in these experiments were to determine which geotextiles: 1) prevent organisms from moving up through the geotextile into the overlying sand, 2) clog or remain permeable to water, and 3) allow **sediments** to move into the sand. Each trial using 6 permeameters ran for one week. The experiment followed a completely crossed factorial design involving two types of stream **sediments** (sandy vs more organic, finer stream bed materials), two types of geotextile patches, and live organisms vs killed controls. Combinations of t Treatments reatments were randomly assigned to trials and permeameters.

We wanted to test two non-woven geotextiles (Amoco #4512 and Amoco #4553) as sediment filters and biointrusion barriers in a controlled laboratory setting, which would simulate water flow in a gaining stream system. Therefore, the permeameters were designed so water would move upward through sediment, then through a geotextile into the overlying water column.

In the area where the test patches were placed there are two main types of sediment, a fairly firm, sandy type near the center of the channel and a very soft, organic rich type near the banks of the channel. We wanted to repeat the combinations of the two sediment types, two geotextile types and two geotextile function types (sediment filtration and biointrusion barrier) three times. A random number table was developed to randomize the sampling. Four trials were conducted, with six permeameters used in each trial.

Acrylic permeameters were used which were in five segments with the bottom segment alone and the middle two and the top two segments permanently connected. An influent hole was made in the bottom segment and an effluent hole was made in the top segment of each permeameter. The influent hole had a ⅛ inch Tygon tube leading into it from a holding tank with a constant water level elevation (or head) fed by tap water. The tank had six tubes attached to the bottom of the tank; each went to a permeameter. Air was bubbled through the water in the tank to remove chlorine. Chlorinated tap water would have adverse effects on organisms, such as death. The residence time of water in the holding tank varied for each set of trials due to the different permeabilities of the sediment combinations in each trial. However, the average residence time was found to be approximately 9.5 minutes. Since organisms were found to move through geotextile in three of the four trials, the bubbling of air through the water removed enough chlorine to sustain life. The effluent hole in each permeameter had a ⅛ inch Tygon tube leading to a filter, which collected the sediment that passed through a geotextile.

Sediment cores were collected directly into the lower pair of segments used in the permeameters. The segments were sealed with stoppers and promptly returned to the laboratory. Cores that were to be used for a permeameter testing a geotextile's efficacy as a biointrusion barrier went directly into a refrigerator, which had a thermostat control placed at 40° F. The experiment was conducted from March through early May of 2002 when the stream and sediment temperatures were very close to this constant temperature. This prevented shock and death of organisms contained within the sediment samples due to rapid increase in temperature. Cores that were to be used for a permeameter testing a geotextile's efficacy as a sediment filter were boiled for 15 minutes to kill any organism in the core to prevent them from getting through the geotextiles and collecting on the filter that was weighed for sediment.

Prior to collecting the cores, filters were weighed on an analytical scale, which has an accuracy of 0.0001 grams. In addition, the specific geotextile that is to be used is placed in the permeameter. On the bottom of the top two sections of the permeameters, a metal disk containing a screen US sieve size 6 is placed in the opening. A geotextile is then placed on the sieve in the opening and sealed around the edge with silicone caulk to prevent anything circumventing the geotextile. The sieve acts as a brace to the geotextile to prevent bowing.

To assemble the permeameters, a metal disk containing a screen US sieve size 270 was placed in the bottom opening of the segments containing the core to support the core and prevent it from falling into the bottom segment. A bead of waterproof adhesive was placed on the top of the bottom segment. The bottom and middle segments were then joined. Similarly, the middle and top segments were attached. In the case of the biointrusion barrier permeameters, 2.5-3.0 centimeters of fine-grained sand was placed in the top segments after the permeameter was fully assembled. This was done to provide a habitat that would sustain organisms that got through the geotextiles. Caps were placed on the permeameters, which were then placed in vice-like vertical frames located in a refrigerator.

Once the permeameters were in place, the influent water tubes and the effluent water tubes were attached using waterproof adhesive. Geotec 0.45 micron glass fiber filters and Whatman GFC 1.0 micron glass fiber filters were positioned at the end of the effluent tubes from permeameters to collect sediment. During the first two trials the Geotec filters were used. It was found that these filters did not maintain their integrity during and after the drying process. Therefore, during trials three and four the Whatman filters were utilized. Once everything was ready, the laboratory-grade demineralized water was turned on and continued to run for seven days

When each week-long trial was over, the water of each permeameter was allowed to collect in separate containers for ½

hour. The water was measured in a graduated cylinder, and flow rates for each permeameter were determined. The permeameters were then taken apart. The segments of the biointrusion barrier permeameters were carefully separated, with the fine white sand above the geotextile placed into one container and the sediment core placed into another container. The **sediments** were preserved so organisms did not degrade and could be enumerated. The filters, which had been collecting sediment from the effluent tubes, were placed in a drying oven at 105 °C for 24 hours. The filters were weighed following drying to determine the mass of sediment collected on them.

In October, 2001, we installed two test patches in an uncontaminated stream. This was part of a test of the geotextile's ability to prevent biointrusion. We sampled four, 3 by 3 meter square patches of stream **sediments** in Gull Creek near Kalamazoo, Michigan, for benthic density. Five core samples (area = 5.07 cm^2 per core) were taken in each patch and preserved with 10% formalin with rose Bengal stain added to facilitate separating invertebrates from the sediment. Two of those areas were subsequently covered with non-woven geotextile patches. The other two areas were experimental controls. The patches were held in place against the current by a 1—2 cm anchoring layer of sand and pea gravel. We have since gone back to inspect the patches and measure the stream velocity. In late April 2002 we sacrificed one randomly selected patch to sample underneath for benthic density. We also measured the benthic density in one randlomly selected control area. Five core samples were taken from each area. In Oct. 2002 we will sample underneath the other geotextile patch as well as in the other three areas to determine the benthic population density.

D. RESULTS AND DISCUSSION

Results of permeameter trials conducted to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in Gull Creek **sediments** (Table 1). Over all trials, the percent of individuals that moved across the geotextile barrier was significantly greater than 0 (mean ± SE: 6.0 ± 1.9; $t_{14} = 5.0$ on arcsine square root transformed proportions, $P < 0.001$). However, in the first trial, we suspected that many of the individuals moved around the geotextile rather than through it, and we modified the permeameters accordingly. Performance of the geotextiles was markedly improved in the remaining trials; only 4.26 ± 2.47% of the individuals present moved through the geotextile ($t_8 = 3.25$, $P < 0.05$). All of the animals that moved through the geotextiles in Trials 2-4 were roundworms or oligochaete annelid worms which, in general, have very small cross-sectional areas. The geotextiles were quite effective barriers against the movement of the remaining infaunal taxa present in the permeamteres, including copepods, ostracods, gammarid amphipods, and chironomid larvae.

Table 1. Percent of animals crossing the geotextile barrier in four laboratory permeameter trials.

Trial	**Permeameter**	Number Below Geotextile	Percent Crossing Geotextile
0	1	32	8.5
	2	25	3.8

	3	15	6.2
	4	29	0
	5	13	18.7
	6	12	14.2
2	2	22	0
	3	16	0
	4	23	8
	6	61	8.9
3	1	11	21.4
	3	17	0
	5	17	0
4	1	18	0
	2	7	0

Field tests of the geotextiles largely support the results of laboratory permeameter experiments. Control and geotextile-covered patches contained a diverse infaunal assemblage in October 2001, immediately before geotextile patches were installed. In all patches, the infaunal community was dominated by copepods, amphipods, oligochaetes, and roundworms (Table 2). Total invertebrate density ranged from 71,441 to 234,057 individuals/m^2. In April 2002, total invertebrate density in the control patch sampled was 69,862 individuals/m^2, with copepods, roundworms, and oligochaete worms accounting for 28.8, 31.1, and 15.8%, respectively, of all individuals. By contrast, the geotextile-covered patch contained only 4359 individuals/m^2 and 2 taxa (roundworms: 65.2%; ostracods: 34.8%) (Table 2). Thus, benthic invertebrate density was reduced by 93.5% in the geotextile-covered patch relative to the control. These results suggest the geotextile provides a highly effective biointrusion barrier. In addition, there was close agreement between the laboratory and field studies in that roundworms, which were more likely to move through the geotextile than other taxa, were best able to maintain populations below the field geotextile barrier. Nonetheless, roundworm density in the geotextile-covered patch was 86% less than that observed in the control patch, indicating that even these animals were strongly affected by the geotextile barrier.

Table 2. Mean invertebrate density (number/m^2) in field patches						
	Oct-01	Oct-01	Oct-01	Oct-01	Apr-02	Apr-02
	Control	Control	Geotextile	geotextile	Control	Geotextile
Taxon	Patch 1 (upstream)	Patch 2 (downstream)	Patch 1 (upstream)	Patch 2 (downstream)	Patch 1 (upstream)	Patch 2 (downstream)
Crustacea						
Copepod (& harpacticoid)	20524.4	80518.8	22103.2	21708.5	20129.7	0
Nauplii	1184.1	19735	0	0	0	0
Cladocera	0	10656.9	0	0	3947	0
Ostracod	3947	3947	1578.8	789.4	6709.9	1578.8
Isopod	6315.2	9867.5	1578.8	4341.7	789.4	0
Amphipod	12630.4	20129.7	33944.2	23287.3	1973.5	0
Insecta						
Chironimidae	11446.3	31181.3	15393.3	5920.5	2368.2	0
Ephemeroptera	1184.1	1973.5	394.7	789.4	0	0
Leptoceridae	0	0	0	394.7	0	0
Zygoptera	0	789.4	0	0	0	0
Elmidae	0	394.7	0	0	0	0
Diptera (misc)	394.7	0	0	0	394.7	0
Other						
Oligochete	13419.8	20129.7	7894	5131.1	11051.6	0
Clam	3157.6	0	394.7	0	789.4	0
Roundworm	26050.2	34733.6	44995.8	9078.1	21708.5	2960.25
Water bear	1184.1	0	0	0	0	0
Collembola	394.7	0	0	0	0	0
TOTAL	101832.6	234057.1	128277.5	71440.7	69861.9	4539.05

D1. target species affected by geotextile barrier

We have applied geotextile barriers to soft **sediments** (sands and finer) because such **sediments** are expected to be the most contaminated. Organisms that live on or in such **sediments** in streams, rivers, and lakes fall into two general

categories: the meiofauna (operationally defined as those animals retained on a 40-μm sieve but pass through a 500-μm sieve) and macrofauna (retained on a 500-μm sieve). Because the maximum pore size in all of the geotextile fabrics that we are testing is < 250 μm, we are most concerned with the ability of the fabrics to constrain movement of the meiofauna. Stream and river meiofauna communities are usually dominated by rotifers (Rotifera), harpacticoid and cyclopoid copepods (Crustacea: Copepoda), small (young) chironomid larvae (Diptera: Chironomidae), naidid and enchytraeid oligochaetes (Annelida: Oligochaetae), and nematodes (Nematoda). All of these groups are well represented in soft **sediments** in Gull Creek (Table 2) and the Kalamazoo River. In addition, ostracods (Crustacea: Ostracoda) are common in many locations. Gammarid amphipods (Crustacea: Amphipoda) often dominate the soft sediment macrofauna in the Kalamazoo River basin, but even juvenile gammarids are too large to pass through geotextile pores, so we do not anticipate the need to be concerned about their movements (although they will be included in both the field and laboratory tests). Because they prey upon microbial communities in the **sediments** and are themselves preyed upon by stream macrobenthos and fish, the meiofauna are important in energy flow in aquatic systems and in linking microbes to large invertebrate predators and fish. Thus, breaking this link should markedly affect rates of PCB bioaccumulation in higher trophic levels.

We predicted that meiofaunal densities below geotextile test patches in Gull Creek would decline rapidly with time since installation and stabilize at very low levels, relative to controls. This prediction has been strongly supported by work conducted thus far (Table 2). Therefore, it appears that the geotextiles should break the microbes – meiofauna – large invertebrates and fish linkage, effectively isolating contaminated **sediments** from the food chain.

E. SUMMARY

Persistent, Bioaccumulative Toxin (PBT)-contaminated **sediments** pose health risks due to contaminant movement up the food chain to fish and humans. PBTs include lead, mercury, **PCBs**, PAHs and certain other organic contaminants. Our goal was to test a new method to cut off contaminated **sediments** from the food chain.

Our method is to cover "hot spots" in the stream or lake bed with an anchored geotextile layer to stop biointrusion and erosion. The permeable geotextile fabric is covered with sand, gravel and/or cobbles to cut off benthic organisms from feeding in the contaminated **sediments**, and prevent erosion of these **sediments** while allowing groundwater inflow. This method can be **combined** with biochemical methods to hasten contaminant degradation beneath the geotextile.

Two geotextiles used as biointrusion barriers were evaluated in laboratory permeameters containing **sediments**; one of the geotextiles was also evaluated in Gull Creek, Michigan. The field trial included four 3 x 3 meter patches in the creek bed. Two of the patches were covered with a geotextile topped with 1-3 cm of anchoring sand and pea gravel; the other two patches were controls. Six months later one of the controls was sampled, and a geotextile patch was sacrificed to permit sampling underneath.

Results of lab and field trials to date suggest that the geotextiles are reasonably effective in preventing the vertical movement of benthic invertebrates in **sediments**. Only 4.26 ± 2.47% of the organisms present moved through the geotextiles ($t_g = 3.25$, $P < 0.05$) in lab Trials 2-4. In Gull Creek, benthic invertebrate density was reduced by 93.5% under the geotextile-covered patch relative to the control after six months of coverage.

These preliminary tests of this new method for reducing health risks from contaminated **sediments** suggest that the geotextile biointrusion barrier has great promise and should be further evaluated in full-scale field trials.

No remedial method, including this one, will solve all problems. Usually several remedial methods are used in concert to deal with real-world problems. It is likely that this proposed method would be most applicable to exposed and/or shallow **sediments** near shore that are vulnerable to erosion. It would probably be applied particularly to PCB hot-spots rather than to entire river or lake bottoms. If the PCB and/or other contaminant concentrations were so high as to result in oily fluids oozing from the **sediments**, dredging would be a more appropriate remedy. The geotextile biointrusion barrier could also be used without oxidants underneath as a temporary or even semi-permanent stabilizing measure to contain **sediments** contaminated with lead, methylmercury, radionucleides and/or **PCBs** until a permanent remedy becomes possible.

II. Chemical/Biological Treatment of PCB-Contaminated Sediments

A. ABSTRACT

In the year since we first received grant funding (March 2001) we have completed all of the year 1 objectives related to **chemical treatment** of **PCBs** with **ozone** and CHEMOX®. Those objectives were to test the feasibility of using **ozone** and CHEMOX® (a proprietary oxidant formerly known as BIOX® that comes in powdered form) to oxidize **PCBs** in laboratory experiments, and to determine the **chemical** nature of the oxidation products and their biodegradability. **Ozone** dosage was also determined. In addition, **ozone** tests were done on two polycyclic aromatic hydrocarbons (PAHs).

The two **PCBs** tested were 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB). The first set of tests was conducted with these two **PCBs adsorbed** to kaolinite. Separate reactors were used for DCB and HCB. **Ozone** was bubbled through, and CHEMOX® was manually mixed into the reactors. The concentrations of the two **PCBs**, Cl^-, and **Chemical** Oxygen Demand (COD) were measured over 30 days of contact time with the two oxidants. After 30 days of contact time with the oxidants, the remaining liquid was separated from the kaolinite and placed in bioreactors containing inoculum from the local wastewater **treatment** plant and nutrients and allowed to reactor for 20 days. Table 1 summarizes the results. In addition, **ozone** tests were done on two polycyclic aromatic hydrocarbons (PAHs).

Table 1. Summary of results for 30 days of treatment of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite with ozone and CHEMOX®, followed by 20 days of biodegradation.

Parameter	Ozone	CHEMOX®
Dichlorobiphenyl (DCB)		
DCB Removed with Oxidants (%)	97 ± 4 (9)[a]	99 ± 4 (9)
Cl^- Released with Oxidants (%)	95 ± 3 (9)	97 ± 5 (9)
Cl^- Released/DCB Removed (mol/mol)	1.9 ± 0.5 (43)	2.1 ± 0.7 (38)
Oxidant Dose (g oxidant/g DCB removed)	18.6 ± 2.7 (43)	NM[b]
COD Removed by Biodegradation (%)	92 ± 5 (9)	97 ± 4 (9)
Hexachlorobiphenyl (HCB)		
HCB Removed with Oxidants (%)	92 ± 6 (9)	95 ± 5 (9)
Cl^- Released with Oxidants (%)	93 ± 4 (9)	96 ± 7 (9)
Cl^- Released/HCB Removed (mol/mol)	6.2 ± 0.9 (43)	6.1 ± 0.7 (43)
Oxidant Dose (g oxidant/g HCB removed)	30.0 ± 3.9 (43)	NM
COD Removed by Biodegradation (%)	91 ± 4 (9)	98 ± 3 (9)

[a] average ± standard deviation (number of measurements).

[b] NM=not measured, because the reactants in CHEMOX® are proprietary.

Treatment with **ozone** and CHEMOX® resulted in greater than 90% removal of both **PCBs**. Removal rates were somewhat greater with CHEMOX® than with **ozone**, and were greater for DCB than for HCB. The percent of Cl^- released with the oxidants was nearly identical (considering statistical variation) to the percent removal of the **PCBs**. Moreover, the molar ratio of Cl^- released to DCB and HCB removed was approximately equal to the number of moles of Cl on the respective **PCBs** (i.e., 2 chlorine/mole DCB, and 6 chlorine/mole HCB). These results indicate that chlorine removal was stoichiometric and complete. The major oxidation products were the same for both oxidants-benzoic acids, formate, and oxylate. The results suggest that Cl atoms on the **PCBs** were replaced with OH groups. The **ozone** dose was approximately 19 g and 30 g per g of DCB and HCB, respectively. Dose was not measured for CHEMOX® because there was no way to measure reactant concentrations, as they are proprietary. Microbes from the wastewater **treatment** plant were able to degrade in excess of 90% of the remaining COD from **treatment** with **ozone** and CHEMOX®, though values were higher for CHEMOX®. Similar results were obtained for ozonation followed by biodegradation of the two PAHs tested.

The effect of humic substances, or native organic matter (NOM), on the dose of **ozone** required to oxidize DCB and HCB was tested in separate laboratory experiments. DCB and HCB were allowed to sorb to fine-grained river **sediments** containing approximately 3% by weight of NOM. These **sediments** were then subjected to the same **ozone treatment** tests as the kaolinite slurries. The doses increased substantially relative to kaolinite. **Ozone** doses in the presence of 3% NOM were approximately 237 g/g DCB and 404 g/g HCB. These doses are approximately 13 times greater than those observed in kaolinite. In addition, approximately 55 days were required to reach the same final DCB and HCB concentrations as were obtained after only 30 days with kaolinite. The increase in oxidant dose would likely be similar for CHEMOX®, though these tests could not be conducted because the oxidant is proprietary.

B. MATERIALS AND METHODS

The goal of this part of the research was to test the feasibility of **ozone** and CHEMOX® as a **chemical treatment** to oxidize **PCBs**, and to characterize the oxidation products and their potential to be biodegraded by common environmental microorganisms. Two **PCBs** were used, 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB). Initial tests with **Ozone** and CHEMOX® were done with DCB and HCB **adsorbed** to kaolinite (i.e., without native organic material, or NOM). Similar ozonation studies were also conducted with polycyclic aromatic hydrocarbons (PAHs), because these compounds are also PBTs and are very typical contaminants of **sediments** in Michigan waterways. In addition, more information is available on ozonation of PAHs than **PCBs**, so conducting side-by-side experiments on both PBTs allows a direct comparison to be made between the results from our PBT ozonation studies and those in the literature. The two PAHs tested were anthracene (a 3-ring PAH) and fluoranthene (a 4-ring PAH). Finally, ozonation studies were conducted with DCB and HCB **adsorbed** to river **sediments** having a NOM content of approximately 3%. This experiment was conducted to compare with results from the kaolinite studies in order to determine the affect of NOM on the dose of **ozone** required to oxidize **PCBs**.

Individual slurries were maintained for each PCB and PAH. All four PBTs were added to achieve an initial concentration in the slurry of 1 g/kg. A phosphate buffer was added to maintain a pH of 7 for the **ozone** experiments and 8 for CHEMOX® experiments, which is a pH range commonly found in **sediments** in the Kalamazoo River. After dosing, the slurries were allowed 4 months of contact time before beginning the ozonation experiments to allow sorption of the **PCBs** to the solids. The slurries were then allowed to settle overnight. The liquid was carefully decanted and 1 L of thickened slurry was placed in 1.5 L glass columns with fritted-glass openings at the bottom to allow gas to be sparged upward through the sediment. The solids content of the thickened slurries was approximately 1.8 kg kaolinite/L and 1.5 kg river sediment/L. The **ozone** reactors were sparged with **ozone** using a laboratory **ozone** generator (OL-100, **Ozone** Services, Burton, British Columbia). The **ozone** generator provided known and fixed O_3 concentrations in the influent gas stream. An on-line O_3 monitor was used to measure **ozone** concentrations exiting the reactor. Effluent air was passed through an activated carbon trap to quantify volatile losses of organic material. Two different O_3 concentrations were tested, 0.5% and 5%, to investigate how **ozone** concentration affected rates of oxidation. Control reactors were sparged with laboratory air. Sparging provided the only mixing, in order to simulate conditions encountered with *in situ* sediment sparging.

For CHEMOX® tests, CHEMOX® was placed in the slurry at a mass ratio of 1:10 (CHEMOX® /soil). The CHEMOX® was mixed into the slurry by sparging with nitrogen gas for an hour every 5 days. CHEMOX® control reactors received no CHEMOX®. Additional control reactors for both oxidants were maintained with kaolinite that did not contain added DCB or HCB, to determine the reaction of the oxidants with kaolinite alone. Each reactor type was run in triplicate. The experiments were conducted at approximately 20°C, at which temperature one mole of gas occupies 24.2 L.

During 30 days of reaction, 5 mL slurry samples were extracted with petroleum ether to measure the parent PBT concentrations. PCB concentrations were then determined using gas chromatography (Hewlett-Packard 5890) with electron capture detection (GC/ECD) and PAHs were quantified using GC (Perkin-Elmer Sigma 300) with flame ionization detection (GC/FID). GC/mass spectroscopy (GC/MS) (Hewlett-Packard 5985B MS) was used to tentatively identify oxidation products of the **PCBs** from **treatment** with **ozone** and CHEMOX®. Identification of oxidation products was not done for the PAHs. The liquid fraction of the slurry (5 mL samples) were analyzed for **Chemical** Oxygen Demand (COD) using the Hach COD test and a Hach DR-4000 spectrophotometer. Chlorine (Cl^-) concentration was also measured (with a Dionex IC) in the reactors containing **PCBs** to quantify the release of chlorine atoms during ozonation.

After 30 days of **ozone treatment**, the reactor liquid was separated from the solids using a centrifuge. Approximately 200 mL of liquid was placed in closed, 500 mL glass BOD bottles with 20 mL of inoculum from the Hamilton, Ontario municipal wastewater **treatment** plant. Nitrogen (NH_4Cl) was added as a nutrient. Phosphorus was already present in the liquid because it was used to buffer the pH in the reactors at 8. Triplicates were run of each reactor. Control reactors received no nitrogen. Oxygen consumption was measured and samples were taken periodically to measure COD. The pH in the bioreactors remained at approximately 8.0-8.2 throughout the entire 20 days of **treatment**.

B.1 Materials

Organic chemicals were obtained from Aldrich (Milwaukee, Wisconsin), including the two **PCBs** 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB), the ozonation products 2-hydroxybenzoic and 2,3,4-trihydroxybenzoic acids and formic and oxalic acids, the extractant diethylether, the extraction surrogate 2-fluorobiphenyl, the derivatizing agent diazomethane, and CH_2Cl_2. Table 1 lists important physical properties of DCB and HCB. Kaolinite, NH_4Cl, K_2HPO_4, KH_2PO_4, HCl, and Na_2SO_4 were from Fisher Scientific (Chicago, Illinois). River sediment was from the Grand River at Brantford, Ontario-Canada. Inoculum was from the aeration tank at the domestic wastewater **treatment** plant in Hamilton, Ontario-Canada.

B.2 Sediment and Slurry Preparation

The river sediment was tested for NOM content and particle size distribution according to *Methods of Soil Analysis*.[20] The river sediment was allowed to settle and the excess water was removed. In 50 L Nalgene® carboys, de-ionized water was used to make separate slurries of kaolinite and river sediment with a solids concentration of approximately 80% on a mass basis. The slurries were buffered at a pH of 7 with equal molar ratios of K_2HPO_4 and KH_2PO_4. The slurries were spiked with DCB and HCB to levels of 1000 mg kg^{-1} and were allowed 4 months with daily agitation of the carboys to provide sufficient time for adsorption of the **PCBs** to the solids. Slurries were thickened by allowing the solids to settle for one week and carefully decanting the liquid. The solids concentrations of the thickened slurries were approximately 1800 kg m^{-3} for kaolinite and 1500 kg m^{-3} for river sediment (i.e., mass of dry solids per volume of slurry). The thickened slurries were then used in the sparging reactors.

B.3 Sparging Reactors

The sparging reactors consisted of 1.5 L glass columns with fritted-glass openings at the bottom to allow gas sparging

upward through the sediment. Each reactor contained 1 dm^{-3} of thickened slurry. Triplicate control reactors were sparged continuously with laboratory air. Triplicate **ozone** reactors were sparged continuously with a laboratory **ozone** generator (**Ozone** Services Model OL-100, Burton, British Columbia, Canada), supplying **ozone** at a fixed concentration of 0.5% (v/v). The gas flow rate in all reactors was 50 cm^3 d^{-1}. Effluent **ozone** concentrations were measured daily with a photometer (Anseros Ozonomat GP, Tübingen, Germany). The daily mass of **ozone** consumed in the reactor was quantified as the difference between the known influent the average effluent concentrations. Effluent gas was passed through activated carbon to quantify stripping of DCB and HCB. The reactors were maintained at 20°C.

The reactors containing kaolinite and river sediment were sparged for 30 days and 55 days, respectively. Periodically 20 cm^3 slurry samples were taken, reactor contents were gently mixed, and pH was measured with a probe. The volume of water lost through evaporation was replaced after each sampling event. Slurry samples were centrifuged for 10 min at 10,000 rpm. The supernatant was filtered (0.45 μm) and soluble **chemical** oxygen demand (COD) and Cl^- were analyzed in quadruplicate sub-samples. The soil pellet was placed under suction on a 0.45 μm filter to remove as much water as possible. The moisture content was then determined on 3 to 4 g samples according to *Methods of Soil Analysis*.[20] Anhydrous Na_2S0_4 was added to absorb remaining water. Quadruplicate sub-samples were taken for extraction and analysis of **PCBs**. Activated carbon was prepared in the same way. After sparging a 30 cm^3 sample was centrifuged and filtered to characterize oxidation products that had accumulated in the aqueous phase.

B.4 Bioreactors

After 30 days of **ozone** sparging, the remaining contents from each reactor (approximately 650 cm^3) were separated from the solids by centrifuging. The liquid fraction (approximately 200 cm^3) was placed in closed, 500 cm^3 glass bottles with 20 cm^3 of inoculum. The biomass concentration of the inoculum was measured using *Standard Method* 2540-D.[21] Nitrogen was added as NH_4Cl, at a mass ratio of 4 g N per g of COD. Phosphorus was added as equal molar ratios of K_2HPO_4 and KH_2PO_4 (0.4 g P per g COD) as a nutrient and to buffer at pH 7. Nutrients and inoculum were added to liquid from two of the three **ozone**-sparged reactors, and the third (a control) received no amendments. The bottles were attached to a Hach BODTrak® to monitor O_2 consumption. Periodically, pH was measured with a probe and 10 cm^3 samples were taken and filtered (0.45 μm) to measure COD. The bioreactors were maintained for 20 days.

B.5 Analytical Methods

DCB and HCB were quantified in quadruplicate 3 to 4 g samples of prepared sediment and activated carbon. **PCBs** were extracted from the samples by adding 10 cm^3 of diethylether and shaking intensely for 1 hour. 2-fluorobiphenyl dissolved in diethylether (0.5 cm^3 of a 2000 g m^{-3} solution) was added as an extraction surrogate. DCB and HCB were quantified using gas chromatography (GC) with electron capture detection (ECD). Two mm^3 of diethylether extract were injected in a Hewlett-Packard 5890 GC with a DB-5 column from J&W Scientific (30 m x 0.32 mm). The injector temperature was 265°C. He flow was 1 cm^3 min^{-1}. The temperature profile was 2 min at 100°C, 8°C min^{-1} to 270°C, 3 min holding, and 24°C min^{-1} to 300°C, 10 min hold. Recovery of 2-fluorobiphenyl was in excess of 95%. Maximum rates of disappearance of DCB and HCB were measured with linear regression analysis.

GC/mass spectroscopy (GC/MS) was used to identify products of PCB reaction with **ozone** and CHEMOX® in duplicate 10 cm^3 filtrate samples from the reactors. The samples were first acidified to a pH of 2 with HCl. The water was extracted three times with CH_2Cl_2. The aqueous layer was discarded and the CH_2Cl_2 was reduced to a volume of 4 cm^3 under a gentle N_2 gas stream. The reduced samples were derivatized with diazomethane and then reduced to 4 mm^3. Solutions (1 molar) of 2-hydroxybenzoic acid and 2,3,4-trihydroxybenzoic acid, formic acid, and oxalic acid were made with de-ionized water and prepared in the same way. Injections (2 mm^3) were done in splitless mode on a

Hewlett-Packard 5890 GC with the column described above. The temperature profile was 30°C to 170°C at 3°C min^{-1}, 10°C min^{-1} to 250°C, and 20°C min^{-1} to 290°C with a 20 min hold. The MS was a Hewlett-Packard 5973 operated in the electron impact mode and scanned between m/z 40 and m/z 250.

Cl^- concentrations were measured in quadruplicate filtrate samples using a Dionex ion chromatograph (IC). A Dionex Ion Pac As11 column (4 mm diameter) was used, followed by a Dionex anion self-regenerating membrane suppressor. With a liquid flow rate of 1.2 cm^3 min^{-1}, the gradient used mixtures of de-ionized water and 2000 g m^{-3} NaOH at the following ratios of water/NaOH: 3 min at 98/2, 5 min at 40/60, 9 min at 0/100, 5 min at 98/2. Soluble COD was measured in quadruplicate 2 cm^3 filtrate samples according to *Standard Method* 5220-D[21], using the Hach COD test (2 g m^{-3} quantification limit) and a Hach DR/4000 Spectrophotometer.

C. RESULTS AND DISCUSSION

C.1 Chemical/Biological Treatment of PBTs

C.1.1 OZONE TREATMENT OF PCBs

The time profiles of the concentration of DCB and HCB in the reactors sparged with **ozone** are shown in Figure 1. The control reactors sparged with air maintained the initial DCB and HCB concentrations of 1000 mg/kg and showed essentially no removal of either PCB over the 30 day period. In contrast, the reactors sparged with **ozone** showed a considerable decrease in concentration of both DCB and HCB. The final concentration, after 30 days, of DCB and HCB were approximately 30 mg/kg and 60 mg/kg, respectively. Sparging with air (in the controls) or **ozone** at a concentration of 0.5% would cause essentially the same stripping of DCB and HCB. Furthermore, DCB and HCB are highly non-volatile. Since no measurable stripping occurred with air sparging, it can be concluded that the reduction in PCB concentrations was the result of reaction with **ozone**. This conclusion is supported by a decrease in **ozone** concentration measured across the reactors (data not shown), which shows that **ozone** was being removed via reaction. Control reactors containing kaolinite with no added DCB or HCB showed essentially no reaction with **ozone**, further indicating that **ozone** reacted with the **PCBs**. Hence, it can be concluded that the loss of DCB and HCB shown in Figure 1 was due to reaction with **ozone**.

Figure 2 shows the production of COD dissolved organic carbon in the reactors during sparging with **ozone**. COD is a measure of the dissolved organic carbon present in the liquid. The COD value of the original slurry was zero, because DCB and HCB are sparingly soluble and remain sorbed to the kaolinite. An increase in COD represents a conversion of the **PCBs** to soluble organic compounds. COD values in the control reactors sparged with air remained at zero throughout the study period. However, COD accumulated in the reactors sparged with **ozone**. Maximum values occurred between 14 days and 18 days. After this time, COD values began to decrease, which can be explained by further oxidation of the initial oxidation products via reaction with **ozone**. Samples of liquid from the reactors were taken after day 30 to identify the ozonation products with GC/MS. The results showed that the predominant compounds comprising the COD were hydroxylated benzoic acids, oxylate, formate, and acetate. These products are known to be biodegradable. No chlorinated compounds were identified in the liquid. The presence of hydroxyl groups on the benzoic acids indicates that reaction with **ozone** replaced Cl atoms on the **PCBs** with OH. Ring cleavage also must have occurred to form the organic acid products identified with GC/MS. Results from other investigations treating chlorinated organics with **ozone** or other oxidants that produce hydroxyl free radicals (e.g., Fenton's Reagent) show that the C-Cl bonds are labile, and that Cl is readily replaced with hydroxyl groups (Heinzle et al., 1995). The accumulation of COD in the **ozone**-sparged reactors indicates that the oxidation products were not nearly as susceptible to attack by **ozone** as were the original **PCBs**.

Figure 3 shows the concentration of chloride ion (Cl^-) in the reactors during **ozone** sparging. The control reactors maintained a Cl^- concentration of zero throughout the 30 days. Control reactors containing kaolinite but no PCB (data not shown) had zero Cl^- concentrations throughout the period, as would be expected. In contrast, the Cl^- concentration in the **ozone**-sparged reactors increased steadily throughout the study period. These results, when considered with those shown in Figures 1 and 2, show that Cl^- was released from DCB and HCB during **treatment** with **ozone**. The GC/MS

results indicate that Cl^- atoms were replaced with OH groups, as discussed above. These results also suggest that measuring the Cl^- concentration in future studies could be used as a surrogate measure of removal of **PCBs** by reaction with **ozone**.

The change in COD concentrations with time in the bioreactors treating **PCBs** already reacted with **ozone** is shown in Figure 4. The initial concentrations of COD in the bioreactors are similar to the final COD concentrations in the **ozone**-sparged reactors (see Figure 2). Slight dilution did occur from addition of inoculum from the wastewater **treatment** plant and nitrogen (approximately 30 mL added to 300 mL of effluent from the **ozone**-sparged reactors). Control reactors received no nitrogen, and these reactors showed no decrease in COD with time. Nor did the control reactors show significant uptake of oxygen (data not shown) except for that exerted by endogenous respiration of the microorganisms present in the inoculum. The active reactors (with added nitrogen) showed a considerable decrease in COD with time. Since the bottles were closed, stripping could not be a mechanism for COD reduction in the active bioreactors. Moreover, oxygen uptake (data not shown) was high in the active reactors, and decreased sharply on day 16 when the COD removal decreased. These results support the conclusion that products of PCB reaction with **ozone** are readily degradable under aerobic conditions. These results are consistent with those of Aronstein and Rice (1995) and Carberry and Yang (1994) who reported that products of oxidation of **PCBs** with Fenton's Reagent are readily biodegradable.

Figure 1. Removal of DCB and HCB resulting from ozone sparging.

Figure 2. Production of COD during ozone sparging of DCB and HCB.

Figure 3. Chloride ion release during ozone sparging of DCB and HCB.

Figure 4. COD removal in bioreactors treating oxidation products of DCB and HCB from reaction with ozone.

The results from the ozonation and biodegradation of DCB and HCB are summarized in Table 2. The removal of DCB was 97% after 30 days, compared with 92% for HCB. The lower removal of HCB may be due to its lower aqueous solubility than DCB. The concentration of O_3 in the reactors had no impact on the removal of DCB and HCB, indicating that rates of reaction with O_3 were limited by desorption of **PCBs** from the kaolinite. Removal of approximately 2 and 6 chlorine atoms from dichlorobiphenyl and hexachlorobiphenyl, respectively, shows that chlorine atoms were stoichiometrically (i.e., completely) removed from the **PCBs** during ozonation. Close agreement between percent removal of the two **PCBs** and percent Cl^- released also indicates stoichiometric removal of chlorine atoms from the **PCBs** by **ozone**. These results suggest that ozonation replaced chlorine atoms in the **PCBs** with hydroxyl (OH) groups, and that ring cleavage also occurs. The **ozone** dose was approximately 19 g and 30 g per g of DCB and HCB, respectively. COD reduction in the bioreactors was in excess of 90%, which shows that the ozonation products of DCB and HCB are readily biodegradable. Furthermore, COD accumulated during ozonation (see Figure 2), which indicates that the partial oxidation products were not nearly as susceptible to attack by **ozone** as were the original **PCBs**.

Table 2. Summary of results for 30 days of ozone sparging of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite, followed by 20 days of biodegradation.

Dichlorobiphenyl (DCB)	
DCB Removed with **Ozone** (%)	97 ± 4 (9)[a]
Cl^- Released with **Ozone** (%)	95 ± 3 (9)
Cl^- Released/DCB Removed (mol/mol)	1.9 ± 0.5 (43)
Ozone Dose (g **ozone**/g DCB removed)	18.6 ± 2.7 (43)
COD Removed by Biodegradation (%)	92 ± 5 (9)
Hexachlorobiphenyl (HCB)	
HCB Removed with **Ozone** (%)	92 ± 6 (9)
Cl^- Released with **Ozone** (%)	93 ± 4 (9)
Cl^- Released/HCB Removed (mol/mol)	6.2 ± 0.9 (43)
Ozone Dose (g **ozone**/g HCB removed)	30.0 ± 3.9 (43)
COD Removed by Biodegradation (%)	91 ± 4 (9)

[a] average ± standard deviation (number of measurements).

Aronstein and Rice (1995) obtained similar results using Fenton's reagent to treat **PCBs**. In this study, Fenton's reagent increased the overall amount of **PCBs** degraded by 4 times relative to sediment samples not treated with Fenton's reagent. Their study also showed that the partial oxidation products were highly soluble compared with the parent **PCBs**. This study showed that chlorine atoms on the **PCBs** were replaced by hydroxyl groups during ozonation. Heinzle et al. (1995) also observed stoichiometric chlorine replacement with OH groups during ozonation of chloroguaiacols (i.e., chlorinated methoxy phenols). Heinzle et al (1995) also observed ring cleavage, and a 10-fold increase in biodegradation of the partial oxidation products compared with the original chloroguaiacols. The stoichiometric replacement of chlorine with hydroxyl groups means that **ozone** dose increases with increasing degree of chlorination on the **PCBs** (Table 1). The fact that hexachlorobiphenyl used approximately three times more **ozone** than dichlorobiphenyl, and that the molar ratio of O_3 consumed/PCB consumed was also about 3 times greater for HCB than DCB suggests that **ozone** is used to achieve complete dechlorination. Heavily chlorinated **PCBs** would then exert a high **ozone** demand. Marvin et al. (1998) reported preferential oxidation of chlorinated compounds (pentachlorophenol) to non-chlorinated organics (PAHs) with **ozone**. Non-chlorinated organic wastes exert **ozone** demands ranging from approximately 4-5 g O_3/g COD (Narkis and Schneider-Rotel, 1980; Jones et al., 1985). The identification of hydroxylated benzoates in the residual COD in these studies is also consistent with advanced oxidation of **PCBs** reported by Brubaker and Hites (1998). These results clearly indicate that **treatment** with **ozone** and CHEMOX® are consistent with those of Aronstein and Rice (1995) and Carberry and Yang (1994) who reported that products of oxidation of **PCBs** with Fenton's Reagent are readily biodegradable.

C.1.2 EFFECT OF NOM ON **OZONE TREATMENT** OF **PCBs**

The effect of the presence of NOM on the **ozone** dose required to achieve oxidation of **PCBs** in **sediments** was determined by measuring DCB and HCB concentrations with time in the river **sediments** having a 3% NOM content. The concentrations of DCB and HCB were measured with time in an **ozone**-sparged reactor, as well as the difference in **ozone** concentration across the reactors. The **ozone** doses required to achieve PCB removal in the river **sediments** similar to those observed in kaolinite were 237 g/g DCB and 404 g/g HCB. These doses are approximately 13 times greater than those observed in kaolinite. The results also showed that approximately 55 days of **ozone** sparging were

required in the river **sediments** to achieve the same removal of DCB and HCB that were obtained in kaolinite slurries. in 30 days. It is known that NOM scavenges oxidants of any kind (i.e., Fenton's Reagent, hydrogen peroxide, permanganate, etc.). NOM is of concern because it increases the required dose of oxidant and the time required to achieve a given cleanup level, and therefore increases the cost of remediation.

C.1.3 **OZONE TREATMENT** OF PAHs

The results from the ozonation and biodegradation of anthracene (a 3-ring PAH, MW=178) and fluoranthene (a 4-ring PAH, MW=230) are summarized in Table 3. The removal of anthracene and fluoranthene by **ozone treatment** was 99% and 94%, respectively. The slightly lower removal of fluoranthene may have been a result of its lower aqueous solubility. The mass ratio of O_3 consumed/PAH removed was slightly higher for fluoranthene (6.4) than for anthracene (7.1). These values are consistent with those reported for ozonation of oil shale wastewaters (Jones et al., 1985; Clayton, 1998). In excess of 95% of the residual COD from **ozone treatment** of both PAHs was biodegraded under aerobic conditions. These results are similar to those obtained by several other studies (Brown et al., 1997; Nelson et al., 1997; Marvin et al., 1998). Ozonation products were not identified for the PAHs. Fluoranthene removal was less that that observed for anthracene. Using a higher **ozone** concentration during sparging had no measurable effect on rate and extent of removal of either PAH, which suggests that the rate of desorption from the kaolinite limited the rate of removal via ozonation. This may be due to the greater hydrophobicity of fluoranthene, which gives it a greater tendency to sorb to the solids than anthracene. This trend was also observed for the two **PCBs** tested.

Table 3. Summary of results for 30 days of ozone sparging of anthracene and fluoranthene, followed by 20 days of biodegradation.

Anthracene	
Anthracene Removed by **Ozone** (%)	99 ± 1 (3)[a]
Ozone Dose (g **Ozone**/g Anthracene Removed)	6.4 ± 0.5 (3)
COD Removed by Biodegradation (%)	96 ± 6 (3)
Fluoranthene	
Fluoranthene Removed by **Ozone** (%)	94 ± 7 (3)
Ozone Dose (g **Ozone**/g Fluoranthene Removed)	7.1 ± 0.4 (3)
COD Removed by Biodegradation (%)	98 ± 5 (3)

[a] average ± standard deviation (number of measurements).

C.1.2 CHEMOX®

The results for CHEMOX® were generally very similar to those obtained with **ozone**. The time profiles of the concentration of DCB and HCB in the reactors treated with CHEMOX® are shown in Figure 5. The control reactors sparged without CHEMOX® maintained the initial DCB and HCB concentrations of 1000 mg/kg to 1100 mg/kg and showed essentially no removal of either PCB over the 30 day period. In contrast, the reactors with CHEMOX® showed a considerable decrease in concentration of both DCB and HCB. The final concentrations of DCB and HCB were both below 100 mg/kg. DCB and HCB are highly non-volatile, and no measurable stripping occurred with nitrogen sparging. Hence, it can be concluded that the reduction in PCB concentrations was the result of reaction with CHEMOX®. This conclusion cannot be supported by a decrease in concentration of the reactants, because CHEMOX® is a proprietary product.

Figure 6 shows the production of COD dissolved organic carbon in the reactors during reaction with CHEMOX®. The COD value of the original slurry was zero, because DCB and HCB are sparingly soluble and remain sorbed to the kaolinite. An increase in COD represents a conversion of the **PCBs** to soluble organic compounds. COD values in the control reactors without CHEMOX® remained at zero throughout the study period. However, COD accumulated in the reactors treated with CHEMOX®. Maximum values occurred between 14 days and 20 days. After this time, COD values began to decrease, which can be explained by further oxidation of the initial oxidation products via reaction with CHEMOX®. Samples of liquid from the reactors were taken after day 30 to identify the oxidation products with GC/MS. The results showed that the predominant compounds comprising the COD were hydroxylated benzoic acids, oxylate, formate, and acetate. These products are the same as those obtained with **ozone treatment**, and are known to be biodegradable. No chlorinated compounds were identified in the liquid. The presence of hydroxyl groups on the benzoic acids indicates that reaction with CHEMOX® replaced Cl atoms on the **PCBs** with OH. Ring cleavage also must have occurred to form the organic acid products identified with GC/MS. Results from other investigations treating chlorinated organics with oxidants that produce hydroxyl free radicals (e.g., Fenton's Reagent) show that the C-Cl bonds are labile, and that Cl is readily replaced with hydroxyl groups (Heinzle et al., 1995). The accumulation of COD in the reactors containing CHEMOX® indicates that the oxidation products were not nearly as susceptible to attack by **ozone** as were the original **PCBs**. The final COD values after **treatment** with CHEMOX® 30 days were approximately 1000 mg/L greater than those observed with **ozone treatment** (cf. Figures 2 and 6).

Figure 7 shows the concentration of chloride ion (Cl^-) in the reactors during **treatment** with CHEMOX®. The control reactors maintained a Cl^- concentration of zero throughout the 30 days. In contrast, the Cl^- concentration in the CHEMOX®-treated reactors increased steadily throughout the study period. These results, along with those shown in Figures 5 and 6, show that Cl^- was released from DCB and HCB during **treatment** with CHEMOX®. The GC/MS results also indicate that Cl^- atoms were replaced with OH groups. These results also suggest that measuring the Cl^- concentration in future studies could be used as a surrogate measure of removal of **PCBs** by reaction with oxidants such as **ozone** and CHEMOX®.

The change in COD concentrations with time in the bioreactors treating **PCBs** already reacted with CHEMOX® is shown in Figure 8. The initial concentrations of COD in the bioreactors are similar to the final COD concentrations in the CHEMOX®-treated reactors (see Figure 6). Slight dilution did occur from addition of inoculum from the wastewater **treatment** plant and nitrogen (approximately 30 mL added to 300 mL of effluent from the CHEMOX®-treated reactors). Control reactors received no nitrogen, and these reactors showed no decrease in COD with time. Nor did the control reactors show significant uptake of oxygen (data not shown) except for that exerted by endogenous respiration of the microorganisms present in the inoculum. The active reactors (with added nitrogen) showed a considerable decrease in COD with time. Since the bottles were closed, stripping could not be a mechanism for COD reduction in the active bioreactors. Moreover, oxygen uptake (data not shown) was high in the active reactors, and decreased sharply on day 16 when COD removal decreased. These results support the conclusion that products of PCB reaction with CHEMOX® are readily biodegradable under aerobic conditions.

Figure 5. Removal of DCB and HCB resulting from CHEMOX®-treatment.

Figure 6. Production of COD during CHEMOX®-treatment of DCB and HCB.

Figure 7. Chloride ion release during CHEMOX®-treatment of DCB and HCB.

Figure 8. COD removal in bioreactors treating oxidation products of DCB and HCB from reaction with CHEMOX®.

The results from the CHEMOX® **treatment** and biodegradation of DCB and HCB are summarized in Table 4. The removal of DCB was 99% after 30 days, compared with 95% for HCB. The lower removal of HCB may be due to its lower aqueous solubility than DCB. Removal of nearly 2 and 6 chlorine atoms from dichlorobiphenyl and hexachlorobiphenyl, respectively, shows that chlorine atoms were stoichiometrically (i.e., completely) removed from the **PCBs** during CHEMOX® **treatment**. Close agreement between percent removal of the two **PCBs** and percent Cl^- released also indicates stoichiometric removal of chlorine atoms from the **PCBs** by CHEMOX®. These results suggest that CHEMOX® replaced chlorine atoms in the **PCBs** with hydroxyl (OH) groups, and that ring cleavage also occurs. COD reduction in the bioreactors was in excess of 97% for both **PCBs**, which shows that the products of reaction of DCB and HCB are readily biodegradable. Furthermore, COD accumulated during CHEMOX® **treatment** (see Figure 6), which indicates that the partial oxidation products were not as susceptible to attack by CHEMOX® as were the original **PCBs**.

Table 4. Summary of results for 30 days of CHEMOX® treatment of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite, followed by 20 days of biodegradation.

Dichlorobiphenyl (DCB)	
DCB Removed with CHEMOX® (%)	99 ± 4 (9)
Cl^- Released with CHEMOX® (%)	97 ± 5 (9)
Cl^- Released/DCB Removed (mol/mol)	2.1 ± 0.7 (38)
COD Removed by Biodegradation (%)	97 ± 4 (9)
Hexachlorobiphenyl (HCB)	
HCB Removed with CHEMOX® (%)	95 ± 5 (9)
Cl^- Released with CHEMOX® (%)	96 ± 7 (9)
Cl^- Released/HCB Removed (mol/mol)	6.1 ± 0.7 (43)
COD Removed by Biodegradation (%)	98 ± 3 (9)

[a] average ± standard deviation (number of measurements).

D. SUMMARY

The results from the **chemical treatment** studies clearly show that:

- **treatment** of PBTs with **ozone** and CHEMOX® decreased PBT concentrations in soil,

• stoichiometric removal of chlorine atoms accompanied removal of DCB and HCB by **treatment** with **ozone** and CHEMOX®,

• the residual organic carbon after **treatment** of PBTs with **ozone** and CHEMOX® was readily biodegradable,

• **treatment** of PBTs with **ozone** and CHEMOX® increased the aqueous solubility of the residual organic carbon relative to the parent compounds,

• NOM increases the dose of oxidant required to achieve PBT removal because NOM scavenges both **ozone** and CHEMOX®.

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